

Technical Summary for Corrosion and Corrosion Prevention Technology: Revisiting the Fundamentals and Looking Forward

The global cost of corrosion in 2020, as estimated using the Uhlig method¹, is approximately 3 trillion USD, which accounts for 3.5% of total global gross domestic product. This number is in approximate agreement with other estimation methods^{2,3} and on a percentage-of-GDP basis, has remained approximately constant for several decades^{4,5}. Depending on the specific method for partitioning global GDP, it can be argued that corrosion is the single largest contributor to global expenditure, which is sensible given the general nature of corrosion as a degradation process which necessitates continual replacement and renewal of metallic structures.

In the United States, the cost of corrosion is approximately 450 billion USD per year and is a topic of great political interest with bipartisan support. Recent movement towards urban and infrastructural renewal has led to an increase in research and development funding for corrosion prevention technology, and to a lesser degree, research into the fundamentals of corrosion science^{6,7}. The effort has not lagged in other parts of the world, especially in industrializing economies with climates favorable towards corrosion⁸.

This trend towards increased focus on corrosion prevention has been slow but steady, and to external observer, inevitable. Multiple review and estimation studies have concluded that between 15% to 35% of the total cost of corrosion can be profitably prevented using existing technologies^{2,4}, and this number is potentially greater given recent advances in corrosion prevention. With the increase in the absolute total expenditure on metallic goods and structures, there is a strong financial incentive to apply corrosion prevention technology, and by proxy, developing new corrosion prevention products and services.

In chapter 1, I review the chronological development of corrosion research, beginning in 1903 with the work of Whitney⁹ on the corrosion of iron, which provides comprehensive and convincing evidence for the electrochemical origin of corrosion. I then describe the classification of corrosion by the American Society of Mechanical Engineers, provide a brief description of each class of corrosion, and additional classes which has emerged since then^{10,11}. This leads to a brief introduction on the theoretical component of this thesis, including the Poisson-Nernst-Planck¹² and the Butler-Volmer equation¹³, before moving on to specific phenomena which complicate the interpretation of corrosion data, i.e., passivation¹⁴, multiplicity of equilibrium states¹⁵, and nonlocal corrosion¹⁶. Chapter 1 concludes with the observation that most of the key developments in corrosion science occur in between 1931 and 1970, in agreement with the period of peak popularity in corrosion research. These key developments have become an indivisible part of corrosion research, with hundreds of thousands of published works (~90,000 in 2020, according to Google scholar) relying on them to provide clarity and guidance to experimental and theoretical works. However, not all of these developments are cohesive.

Chapter 2 dissects some of these broadly-accepted, yet problematic concepts in corrosion science: crevice corrosion, anode / cathode separation, and differential aeration. Crevice corrosion occurs in occluded geometries where oxygen is enriched at certain positions. For example, a scored iron surface would have higher oxygen concentration at the opening than deep in the scored surface. This enhances oxygen reduction at the opening by shifting the reduction equilibrium. The enhancement of oxygen reduction is also believed to suppress Fe oxidation. To balance oxygen reduction, Fe is oxidized deep in the crevice, resulting in localized corrosion, i.e., rapid corrosion in a small area which then acts as a nucleation point for mechanical failure. This macroscopic separation between the anode and the cathode in the presence of oxidant concentration gradient is known as anode / cathode separation and the phenomenon as a whole is known as differential aeration¹⁷. In brief, I critique differential aeration as applied to flat metallic surfaces of uniform composition on the basis of (1) lack of motive for macroscopic

anode / cathode separation, (2) conflict with existing understanding of corrosion kinetics¹⁸, and (3) false prediction of species mobility. Furthermore, several prominent evidence in support of macroscopic anode / cathode separation on corroding iron surfaces can be explained without reference to anode / cathode separation. Follow-up experimental works suggests that the situation is considerably more complex than expected even for very simple geometries, with evidence for autocatalysis and corrosion-induced migration of precipitated oxides.

In chapter 3, I move on from corrosion science to corrosion prevention technology and explore two related failure mechanisms: osmotic blistering and water absorption / leaching of soluble components. The former builds upon existing understanding of blister formation to arrive at a comprehensive macroscopic model of osmotic blistering. Blisters initiate at locations with low critical adhesion stress and / or high local solute concentration and propagate by growth and / or deformation. Irreversible blister growth occurs when adhesion stress exceeds the critical adhesion stress of the metal / coating pair, and deformation occurs when osmotic pressure exceeds the elastic stress of the coating. If the growth continues unabated, the coating eventually becomes delaminated, and if deformation continues unabated, the coating eventually ruptures. The model has been validated against blister growth data, leading to the development of three dimensionless numbers, each classified according to the source of osmotic pressure, which can be used for engineering design of polymeric coatings capable of resisting visible deformation, rupture, and delamination. However, the model makes simplifying assumptions on coating behavior; to complete the analysis, I turn to water absorption and leaching of soluble components as a description of coating degradation. I develop a semi-continuum poromechanical model where diffusion flux, driven by the concentration gradient within the hydrophilic volume, occurs in conjunction with elastic relaxation flux, driven by the wetting of hydrophilic volume. The mobility of the elastic relaxation flux is derived from the linear nonequilibrium dynamics of a semi-permeable membrane. The resulting model is used to analyze experimental water uptake and ion leaching data and validated against mass balance closure.

In chapter 4, I apply machine learning and high-throughput experimentation for the design of anti-corrosion coatings. This chapter focuses on the construction of the experimental setup, considerations and methods for reducing data requirement, and the electrochemical method of choice, i.e., electrochemical impedance spectroscopy (EIS). As an illustration, the application of EIS for the analysis of an interdigitated vanadium redox flow battery is provided. This chapter places considerable emphasis on the experimental procedure and the learning points obtained through trial-and-error on several prototypes.

In chapter 5, I discuss the analysis of the EIS data of the kind used in chapter 4. The success of EIS data analysis is contingent on the ability to express the system as a quantitative physical model, but it is often the case that the system is not sufficiently well-understood to allow such a model to be written. In such cases, the distribution of relaxation time (DRT) problem may be solved, wherein the underlying model is assumed to be a series of relaxation processes with a distribution of characteristic timescales. More recently, the works of Florsch, Revil, and Camerlynck¹⁹ and Song and Bazant²⁰ demonstrate that prior knowledge can be used to construct the underlying physics of an EIS inversion problem, such that the resulting distribution corresponds to an observable, as opposed to a mathematical construct whose utility is restricted to the identification of the number, size, and average timescale of underlying processes. This motivates the idea of a generalized EIS inversion problem, in which the form of the underlying physics is not specified a priori, and the corresponding generalized EIS inversion algorithm, which solves the problem independently from the underlying physics.

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