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Cathodic corrosion

Hersbach, T.J.P.

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Author: Hersbach, T.J.P.

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Summary and Future Outlook

The work in this thesis is centered around cathodic corrosion: a chemical process that severely alters metals, but is significantly less understood than its anodic counterpart. Though cathodic corrosion is still shrouded in unresolved mysteries, this thesis marks an important advance in our understanding of this remarkable chemical phenomenon.

The thesis starts with two chapters that explore the cathodic corrosion behavior of Pt, Rh and Au in 10 *M* NaOH. In Chapter 2, Pt is shown to start cathodically corroding at much milder potentials than previously assumed. Similar findings are reported for Rh and Au in Chapter 3. Both chapters also support an earlier hypothesis regarding the role of cations in controlling the etching preference of cathodic corrosion.

The role of cations is further investigated for Pt, Rh and Au in Chapter 4. This investigation combines elaborate experimental and theoretical characterization to firmly establish the structure-guiding role of cations. Perhaps surprisingly, Chapter 4 suggests an equally important role for adsorbed hydrogen. Based on these findings, the chapter presents the first concrete hypothesis of the key reaction intermediate during cathodic corrosion: ternary metal hydrides.

Such hydrides are evaluated in Chapter 5, which examines Pt nanoparticles during cathodic corrosion, using *operando* “high-energy resolution fluorescence detection X-ray absorption near edge structure” (HERFD-XANES) experiments. This chapter finds that the ternary metal hydride Na₂PtH₆ is a likely candidate for being the enigmatic intermediate. If proven correct in future experimental and theoretical analysis, this would, to our knowledge, be the first detection of this type of hydride in an aqueous environment.

Chapter 2–5 are therefore focused on expanding the available knowledge of cathodic corrosion. Part of this knowledge is applied and elaborated upon in the application-focused Chapters 6 and 7. Chapter 6 illustrates how to optimize catalysts through pre-treatment by cathodic corrosion. Chapter 7 then investigates the known use of cathodic corrosion for creating PtRh nanoparticles. In doing so, valuable clues towards the corrosion behavior of alloys are gained and precautions for alloy nanoparticle production are identified.

As such, the presented chapters build upon previous work on cathodic corrosion. They shed light on previously observed cation effects,¹ and indicate the nature of the metallic anion.² In addition, they add a modest but relevant contribution to the growing body of literature of cathodic corrosion as a method to produce metal and metal oxide

nanoparticles.³⁻⁶ These contributions facilitate the applications of cathodic corrosion and the relatively unexplored chemistry that drives it.

These advances have nonetheless left many questions unanswered and have generated new questions. A pertinent selection of these questions will be presented below.

First of all, the presence of ternary metal hydrides would imply an importance of a hydrogen donor like H₂O. The role of such a donor might be explored by restricting the availability of water. Though the complete exclusion of water is extremely challenging, water-free conditions can be approximated by performing experiments in aprotic solvents or ionic liquids. Mixtures of these solvents with water might also prove useful. The use of non-aqueous solvents will surely generate interesting results regarding the cathodic chemistry of metals and could point towards the reduction of metals towards unexpected species.^{7,8}

Additionally, the existence of ternary metal hydrides would need to be studied for metals other than platinum. Such studies would test the generality of proposed reaction intermediate. This would require spectroscopic studies of Rh and Au, but also systematic cathodic corrosion studies of metals like Ir, Cu and Ag. These metals were not studied in the present work due to challenges in electrode preparation, but the use of larger electrodes and an inductive annealing setup could help overcome these challenges.

Furthermore, this thesis largely focuses on qualitatively understanding cathodic corrosion. This qualitative understanding might enable more quantitative future studies on factors like the corrosion kinetics. Exploring these etching kinetics *ex-situ* or even *in-situ* through methods like electrochemical scanning tunneling microscopy could provide a wealth of information on cathodic corrosion.

A final unresolved question is the role of *anodic* corrosion in nanoparticle formation, when it is combined with cathodic corrosion to create nanoparticles. Though Chapter 7 and previous work² provide initial results on this matter, further carefully designed experiments would be necessary to unambiguously quantify the role of anodic corrosion. Such experiments would require using a three-electrode setup, instead of the two-electrode setup that is commonly used when making nanoparticles.

Answering these questions could help propel cathodic corrosion from being a niche phenomenon to being a useful component of every electrochemist's toolkit. Doing so would not only explore novel chemistry at the cathodic side of the electrochemical series, but would also inspire new approaches to tackling the electrochemical challenges of the 21st century. It is my hope that this thesis has furthered this development of cathodic

corrosion.

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