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Selectivity and competition between the anodic evolution of oxygen and chlorine

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Summary and Outlook

Summary

The work presented in this thesis concerns the electrochemical, anodic evolution of oxygen gas and chlorine gas in an aqueous environment. These two reactions can occur simultaneously in a chloride-containing electrolyte, and they play central roles in several electrochemical processes that are very energy intensive. Their kinetics, and the selectivity between them are therefore of central importance. Only one of the two reactions is usually desired, such as the Chlorine Evolution Reaction (CER) in the chlor-alkali process. On the other hand, only the Oxygen Evolution Reaction (OER) is wanted at the anode during water electrolysis for renewable energy conversion, where ideally seawater is used as a substrate. In either case, any occurrence of the other reaction strongly undermines the feasibility of the overall process. ‘Separating’ the two reactions is an imposing task, because their activities are highly correlated; most catalysts capable of the OER will also oxidize chloride if it is present in the electrolyte. Especially the development of highly desired OER-selective anodes is difficult, because the simpler nature of the CER reaction mechanism implies that it has a kinetic advantage over the OER. This thesis is therefore dedicated to how the OER and CER compete and interact on a very fundamental level, a subject of which surprisingly little research exists, especially regarding dilute chloride solutions.

As selectivity underlines most of this work, in Chapter 2 we first explored a new method for determining chlorine vs. oxygen selectivity using a rotating ring-disk electrode assembly, which is a widespread tool within the electrochemistry research field. A Pt ring fixed at 0.95 V vs. RHE in a solution of pH 0.88 was used to selectively reduce the Cl_2 formed on the disk. Contrary to most established methods for measuring chlorine evolved, this method has short response times and can be used within almost any potential vs. time program. It is accurate enough to deduce fundamental kinetic parameters of the CER proceeding alongside the OER, although it is limited to acidic solutions ($\text{pH} \approx 1$) and moderate current densities. As proof of concept, we used it to show that on a glassy carbon-supported (GC) IrO_x catalyst, the selectivity towards chlorine evolution rapidly approached 100% as the chloride concentration $[\text{Cl}^-]$ increased from 0 to 100 mM. Our results furthermore suggest that on IrO_x , the OER is not suppressed or influenced by the presence of Cl^- or by the CER taking place simultaneously on the surface.

In Chapter 3, we looked deeper into the apparent fundamental link between the OER and CER, by studying the reactions on a series of closely-related iridium-based double perovskites. As has been implied by previous research, we found a strong linear correlation between OER and CER activity on these materials, providing further evidence for the scaling relationship that exists between the OER and CER. We furthermore performed online inductively coupled plasma mass spectrometry (ICP-MS) measurements on these materials, as material stability is also an important issue in the context of OER electrocatalysis. We found indications that catalyst dissolution pathways are very different between the OER and CER. In particular, chloride selectively enhanced the dissolution of the noble metal component. A chloride reaction order analysis was carried out to look at the effect of surface area changes due to

adventitious leaching, and the observed suppressing effect of chloride on the OER. The analysis suggested that the CER mechanism on the double perovskites was notably different from that on IrO_x and semi-crystalline IrO_2 , which were used as reference materials.

Moving on from the study of selectivity and scaling between the OER and CER, we dedicated Chapters 4 and 5 to a deeper investigation of the reaction mechanism of the CER on Pt and IrO_x surfaces. We looked specifically into the effect of bromide, which is a small but important component of seawater, and how the oxidation mechanisms of Br^- and Cl^- may affect each other and the OER. In Chapter 4 the focus was on the parallel Bromine Evolution Reaction (BER) and the CER, using Pt as an electrochemical model system. We found that the oxidation of bromide is hindered by competing chloride adsorption on Pt, in a way that can be quite satisfactorily modelled by a simple Langmuir isotherm describing the competing adsorption and reactivity of all species. The oxidation of chloride was however not properly captured by this same model, and may follow a substantially different mechanism. Furthermore, from voltammetry, in-situ UV-Vis experiments and considerations of solution chemistry and oxidation products that may be expected in a mixed acidic bromide/chloride electrolyte, we found that Pt seems to catalyze the formation of the interhalogen compound BrCl in-between the oxidation of bromide and chloride. Chapter 5 extends the approach introduced in Chapter 4 to GC-supported IrO_x , this time focussing on how the OER is affected by the presence of chloride and bromide, keeping in mind that Ir-based electrocatalysts are more applicable to seawater electrolyzers than Pt. Chloride and bromide also adsorb competitively on IrO_x , but contrary to Pt, we found no evidence of interhalogen BrCl formation. We also found that even a relatively small amount of bromide strongly slows down both the CER and OER, where especially the OER and its selectivity is highly affected. This knowledge can lead to a deeper understanding of the challenges to be faced when developing an OER-selective anode for seawater electrolysis.

In Chapters 6 and 7, we look more deeply into OER-selective anodes, so that electrolysis of readily available seawater may be achieved without the formation of (mainly) chlorine as toxic by-product. In Chapter 6, we first investigated the OER vs. CER selectivity of anodes based on manganese oxide (MnO_x), one of the few types of materials with unusually high OER selectivity. To model this class of catalysts, thin films ($\sim 5\text{--}20$ nm) of MnO_x were electrodeposited on GC-supported IrO_x in aqueous chloride solutions of $\text{pH} \sim 0.9$. Using rotating ring-disk electrode voltammetry and online electrochemical mass spectrometry, it was found that deposition of MnO_x onto IrO_x decreases the CER selectivity of the system in presence of 30 mM Cl^- from 86% to less than 7%, verifying the high OER-selectivity of MnO_x -based catalysts. Interestingly, detailed studies of the CER mechanism and ex-situ structure studies using SEM, TEM and XPS suggest that the MnO_x film is in fact not a catalytically active phase, but functions as a permeable overlayer that disfavors the transport of chloride ions. This approach to enhancing the OER selectivity by selectively preventing chloride from reacting at the anode is explored further in Chapter 7, where we investigated the effect of thin (10–20 nm) overlayer films composed of amorphous silicon oxide (SiO_x), which is an electrochemically inert material resistant to acid. The SiO_x was spin-coated onto Pt and GC-supported IrO_x , as well as on two types of Ti-based anodes using Ir, the latter of which were identical to Ir-based anodes used

on an industrial scale. From the SiO_x/Pt electrode, which served as a proof of concept, it was clear that the silicon-based overlayer can be a very effective barrier against the CER on flat, relatively well-defined surfaces, while still allowing OER activity to occur on the buried platinum at higher potentials. Experiments on $\text{SiO}_x/\text{IrO}_x/\text{GC}$ electrodes, which are more closely related to Ir-based catalysts used in electrolyzers, yielded mixed results. CER activity was again impacted, but so was the OER. More importantly, the CER was not completely suppressed regardless of the thickness of the SiO_x overlayer. SEM/EDS measurements and kinetic analysis suggested that the still significant CER-activity originated from defects in the film. It is likely that the spin-coating procedure used to produce the SiO_x films is not very compatible with rough surfaces when very thin (<20 nm) films are applied. On the other hand, the Ti-based Ir anodes, to which significantly thicker SiO_x films were applied, showed much better CER suppression, with a CER selectivity of roughly 16% in 30 mM KCl. This value is the same order of magnitude as the thickest $\text{MnO}_x/\text{IrO}_x/\text{GC}$ electrodes measured in Chapter 6. The extra thick SiO_x overlayer was applied because the MMOs have micrometer-scale roughness. Besides good OER selectivity, this layer also resulted in rather low electrocatalytic activity. Although these initial results leave room for improvement, it is clear that the concept of buried interfaces may be a promising approach to reach OER-selective water splitting in saltwater electrolyzers. There are still abundant parameters that can be optimized regarding the SiO_x overlayer.

In Chapter 8, we explored methods of reducing ring-disk collection errors during RRDE voltammetry. These errors are caused by formation of gas bubbles during vigorous evolution of gas on the disk electrode, and were pervasive throughout the experiments performed in this thesis. We tried to improve the reliability of the RRDE collection factor by mounting a thin wire close to the surface, to dislodge bubbles that formed specifically on the interface between the disk and the disk-ring spacer. This approach was tested for the detection of chlorine during parallel chlorine and oxygen evolution, and resulted in a notable alteration of the collection efficiency. Its value became lower than theoretical expectations and also quite stable, even under higher current densities. Additionally, the RRDE tip was coated in a hydrophilic polymer, to reduce the tendency of bubble formation. This was tested for the collection of hydrogen and oxygen gas, and led to a mild increase in overall performance. The coating allowed for approximately 50% higher hydrogen evolution current density without ring failure, and for oxygen collection led to an overall improvement in behavior.

Outlook

From this thesis, several perspectives arise on the chlorine vs. oxygen selectivity problem. Primarily, the strong scaling between OER and CER activity would prohibit optimizing the selectivity purely on the basis of kinetic considerations. Apart from specific adsorption effects by chloride ions, the OER and CER seem not very strongly affected by each other, so that their selectivity can be seen as a steady ratio between their intrinsic activities. The CER then kinetically always has the upper hand, while the OER activity is small but non-zero. To improve the selectivity towards a single reaction, this work suggests that chloride mass transport is the most important factor, once effects from specific chloride adsorption are

accounted for. The CER selectivity has been optimized this way with great success in the chlor-alkali industry over the last few decades, by using highly concentrated chloride solutions. Enhancing instead the OER selectivity is certainly more challenging, and also highly desirable as it could enable chlorine-free water splitting in saltwater electrolyzers. The most effective way of achieving this would be to negatively affect chloride diffusion to the surface, compared to that of water. The concept of 'buried interfaces' relating to Chapters 6 and 7 is therefore very promising. Possibly, every highly OER-selective anode previously reported is reliant on this principle. It allows for versatility in the design of electrolyzers, since it effectively decouples the selectivity issue from the OER activity issue. When using buried interfaces to enforce selectivity, there would be no need to find wholly different catalysts for freshwater and saltwater splitting. The overlayer may also increase the mechanical stability of the catalyst, which is an attractive prospect for water electrolysis, where catalyst durability is a major issue. An extra advantage of the permselective overlayer is that it will likely also prevent the adsorption and oxidation of bromide, which may pose a serious problem (see Chapter 5).

Tailoring effective overlayers against the CER is as of yet uncharted territory, with huge potential but with many hurdles and uncertainties to be overcome as well. The material to be used, besides being permselective against chloride, should be chemically and electrochemically inert, and resistant to the harsh conditions of OER electrocatalysis. Judging from Pourbaix diagrams and previous literature, possible candidates in neutral and acidic media at high potentials could be oxides, such as those of Ti, Si, Ce, Sn, W, Mo, or Sb. Alternatively, surface modification with polymers or thin membrane-based approaches could be promising. The layer should be just thick enough to completely block chloride transport over extended times, while also as thin as possible to minimize the impact on the transport of OER-related species to the buried catalyst. Getting the material in position, homogeneously distributed across all active catalytic sites, is one of the main challenges. Ideally, electrodeposition or a deposition method indirectly dependent on current (such as electroflocculation) should be used, as this leads to the most active catalyst sites being specifically targeted. As shown in Chapter 6, another approach could be to have the overlayer precursor present in the bulk solution in dilute quantities, leading to a dynamic deposition/dissolution equilibrium and a guarantee of the overlayer integrity over extended operating times. The bulk precursor concentration, which would determine the driving force for deposition and the equilibrium thickness of the deposited overlayer, should however be chosen carefully to prevent layers of excessive thickness to form and interfere with the electrolysis process.

Although the work presented in this thesis is highly fundamental, it will hopefully offer some guidelines when searching for practical solutions to more efficient separation of the evolution of chlorine and oxygen, especially so for saltwater electrolysis. The notion that mass transport of chloride is the most important (and perhaps only) factor affecting CER selectivity could steer saltwater electrolysis in new research directions. A breakthrough there may give the general research field of hydrogen as energy carrier a welcome push of attention. It may galvanize public and corporate interest into making an energy infrastructure based on electrolysis and fuel cells a reality.