

Foreword

Saving the planet has become a popular topic among chemistry students and faculty alike. Individual steps of the water splitting reaction have been extensively studied at the interfaces of carbon-based nanostructures, notorious for corroding fast, and of noble metal particles, the cost of which is redhibitory for large-scale applications. In this context, Sandra Haschke's materials choice appears all the more consequent and bold: her Master's thesis is dedicated to iron(III) oxide, 'rust', as a platform for electrochemical water oxidation, the kinetic bottleneck of the overall water splitting.

Indeed, iron(III) oxide provides the advantages of wide availability and low cost, as well as thermodynamic stability, two aspects of crucial practical importance. The impediments associated with iron(III) oxide, however, are of fundamental nature: low electrical conductivity and poor catalytic activity. Recent literature precedents have provided approaches to circumventing these difficulties by doping the solid with various transition metal ions in its bulk or at its surface. Variations of the surface morphology on several length scales (1-1000 nm) have repeatedly been invoked to also influence the overall (photo)electrochemical performance via the geometric effects of surface area and transport path lengths, albeit never directly addressed in experiments.

Sandra tackles that geometric aspect in her work. She establishes the preparation of highly ordered nanoporous iron(III) oxide surfaces the geometry of which is accurately defined and perfectly tunable. She characterizes the chemical and morphological changes that take place upon thermal annealing and electrochemical treatment. She demonstrates that a roughened surface translates into improved water oxidation current via the increased specific surface area. She then systematically investigates how electrocatalytic turnover is affected by elongation of the samples' pores, and identifies a clear optimum value. She finally demonstrates that this optimal geometry corresponds to the experimental situation in which charge transport towards the electrode surface and charge transfer at the surface occur on the same timescale.

Thus, this Master's thesis not only stands out in terms of the breadth of methods utilized in the realms of preparation (porous materials, thin films), characterization (microscopic and spectroscopic techniques), and electrochemical investigation. Rather, it impresses by providing a very complete and coherent picture of the factors controlling electrocatalytic turnover at what is initially considered as an unlikely catalyst candidate, but turns out to be a versatile and well-behaved material when appropriately structured. In fact, over the course of

her work, Sandra manages to improve electrocatalytic turnover at iron(III) oxide a thousand-fold. Thereby, she delivers not only a physical-chemical insight of fundamental importance, but also a substantial, quantitative efficiency gain. With this, she puts iron-based materials not quite on par with systems that require much more costly elements, but at least into a range that allows for close comparison — a development of broad significance for chemistry and chemical engineering. In essence, Sandra shows that via clever nanostructuring, rust can be transformed into gold, to some extent...

Prof. Julien Bachmann

Anorganische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg

Electrochemical Water Oxidation at Iron(III) Oxide

Electrodes

Controlled Nanostructuring as Key for Enhanced Water
Oxidation Efficiency

Haschke, S.

2015, XVI, 51 p. 24 illus., Softcover

ISBN: 978-3-658-09286-3