Theoretical electrochemical fluorination

First Principle Investigations of Various Anode Materials for the Simons Process

***Prof. Dr. Beate Paulus, Tilen Lindic**, Institut für Chemie und Biochemie, Freie Universität Berlin*

In Short

- Electrochemical fluorination
- Simons process
- Periodic DFT calculations
- Copper as a possible replacement of nickel anode

Knowingly or unknowingly everyone is using fluorinated organic compounds in their everyday lives. Be it as pharmaceuticals, agrochemicals, battery materials or in any other form of their vast applications.[1] Because of that the fluorination of organic molecules is a topic in chemistry which attracts a lot of interest in research. Traditionally organic molecules were fluorinated by direct fluorination, that is by reaction of fluorine gas with the substrate of interest. This is, however, not a straightforward and easy task, mainly because of the high reactivity and therefore tricky nature of handling fluorine. A huge breakthrough in fluorinating organic molecules was achieved in the middle of 20. century by Simons. He reported an efficient method of fluorination by means of electrochemistry. [2] The process is today known as the Simons process.

Classically the Simons process uses a nickel anode immersed in an anhydrous HF (see figure 1). A typical potential applied in the industrial setup is 5-6 V. The mechanism is not fully understood. The reaction is thought to proceed in two steps. The first one is the oxidation of Ni surface, which is facilitated by the electric current, and subsequent formation of oxidised nickel fluorides Ni_xF_y. The source of the fluorine is the anhydrous HF, which also acts as a solvent. In the second step the fluorination itself occurs. Thermodynamically unstable nickel fluorides react with the organic substrates and form fluorinated organic compounds. In this way a wide variety of organic molecules, even functionalised, can be fluorinated. Some insight in the formation of the Ni_xF_y films and the mechanism of the Simons process has already been achieved in our group. [4]

An interesting, yet fairly unresearched, possibility is the substitution of the nickel anode with another transition metal, for example copper. A possible limitation of using copper as an anode material could be the formation of a non-conducting film on the surface upon the immersion into the anhydrous HF.

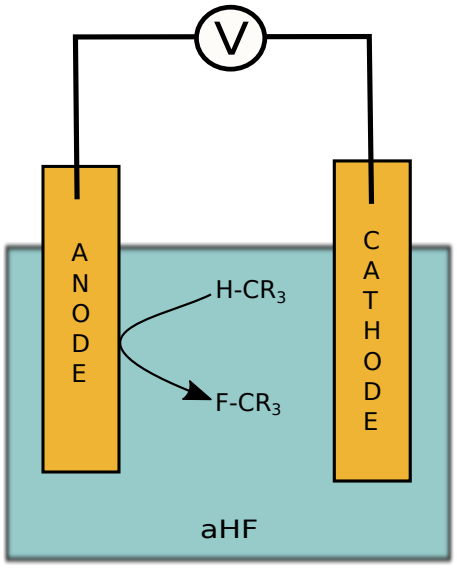

***Figure 1:** Scheme of the Simons process with the mechanism as proposed by Sartori et al.[3]*

[5] Even though this might be experimentally challenging, theoretical investigation could nevertheless provide insight into the mechanism involved in electrochemical fluorination.

For our investigation we intend to use periodic DFT as implemented in VASP.[6] As exchange correlation functional we will use PBE(+U) for structure optimisations and hybrid HSE06 for single point calculations on top of the optimised structures.

Our starting point will be the investigation of CuF_2. In its bulk form CuF_2 adopts distorted rutile structure. As with most of the copper(II) compounds it is highly Jahn-Teller distorted. We would like to investigate the low Miller index surfaces of CuF_2, namely (100), (001), (101), (110), (111), (010) and (011) surfaces. Theoretical investigation of CuF_2 surfaces has, to the best of our knowledge, not yet been reported in the literature in a systematic way. By comparing the results previously obtained for the NiF_2 we also hope to shed some light onto the aforementioned insulating properties of CuF_2. This research could also be interesting for the broader scientific community since CuF_2 is a promising cathode material in batteries. [7]

To understand how CuF_2 is formed on the Cu anode we will investigate the adsorption of F and HF on the Cu(111) surface in a similar way as in [8]. Because

the processes occurring on the anodes are thought to include the physisorption of two HF molecules with the subsequent release of H_2 and chemisorption of F we will use the nudge elastic band (NEB) method to investigate the pathways and hence the kinetics between clean, physisorbed and chemisorbed surfaces.
Our experimental collaborators, who already did similar studies for the Ni anode[4], are also already preparing similar experiments with the Cu anode. Combining together our theoretical and their experimental results we hope to achieve greater understanding of the underlying processes involved in the electrochemical fluorination on various anode materials.

WWW

https://www.bcp.fu-berlin.de/chemie/index.html

More Information

[1] A.M. Thayer, *Chemical & engineering news*, **84**, 15, (2006).

[2] J. H. Simons, W. J. Harland, *Journal of The Electrochemical Society*, **95**, 55 (1949). doi:10.1149/1.2776733

[3] P. Sartori, N. Ignat'ev, *Journal of fluorine chemistry*, **87**, 157 (1998) doi:10.1016/S0022-1139(97)00139-5

[4] S. Mattsson, G. Senges, S. Riedel, B. Paulus, *Chemistry - A European Journal* (2020). doi:10.1002/chem.202000881

[5] N. Hackerman, E. S. Snavely Jr, L. D. Fiel, *Corrosion Science*, **7**, 39 (1967). doi:10.1016/S0010-938X(67)80068-4

[6] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **54**, 11169 (1996). doi:10.1103/PhysRevB.54.11169

[7] D. T. Thieu, et al., *Advanced Functional Materials*, **27**, 1701051 (2017). doi:10.1002/adfm.201701051

[8] S. Mattsson, B. Paulus, *Physical Chemistry Chemical Physics* **22**, 4407 (2020). doi:10.1039/C9CP06348J

Project Partners

AG Riedel

Funding

SFB 1349 Fluor-Spezifische Wechselwirkungen