

Modeling electrochemical fluorination using first principles

First principle investigations of electrochemical fluorination on nickel anodes

S. Mattsson, B. Paulus, *Institut für Chemie und Biochemie, Freie Universität Berlin*

In Short

- Fluorinated nickel surfaces
- Mechanism of fluorination
- Modeling electrochemical fluorination
- Density functional theory

Fluorinated organic compounds are used in a wide selection of applications, for example in functional materials and pharmaceuticals.[1] Classically, fluorination was done by using elemental fluorine as reagent, in so called direct fluorination. Electrochemical fluorination (ECF) provides an alternative to direct fluorination, and is manifested in the Simons process.[2] The main compartment of the cell is a nickel anode, on which the fluorination step occurs. Anhydrous hydrogen fluoride (HF) is crucial to the reaction, since it acts as solvent, as well as fluorine source. A schematic picture of the Simons process is shown in Figure 1.

The mechanism of the Simons reaction has to this day been studied relatively little, but has been proposed to consist of two main steps:[3] 1) the electrochemical step; oxidation of the Ni surface made possible by the current, and subsequent formation of a layer of higher oxidized nickel fluoride Ni_xF_y (e.g. NiF_3 , NiF_4 , Ni_2F_5) where HF is the source of F^- anions. 2) the fluorination step; reaction of the thermodynamically unstable Ni_xF_y with organic compounds, leading to fluorinated products.

Our primary goal is to investigate the Ni_xF_y mechanism using density functional theory (DFT) with

periodic boundary conditions. The reaction is non-spontaneous in the absence of an electric potential, why atomistic scale DFT calculations must be put in a context with proper electrochemical models. Nørskov and coworkers have developed an approach to complement DFT with an introduced potential to calculate reaction energies.[4]

To apply that method, we face the greater challenge of a proper description of the structure of the Ni/Ni_xF_y film. Of the nickel fluorides, only the non-reactive NiF_2 has been well characterized by experiments, whereas some data exists on NiF_3 , which is believed to be analogous to the experimentally more studied CoF_3 . Both trifluorides are powerful fluorinating agents.[5] CoF_3 is frequently used in laboratory work, while NiF_3 is thermodynamically instable and decomposes to NiF_2 and fluorine gas. The other candidate Ni_2F_5 also has been very little studied and no crystal structure has been proposed. In this work, we want to compare bulk and surface properties of NiF_2 and NiF_3 with CoF_2 and CoF_3 , as a first step for more complicated models of the Ni_xF_y films.

We also intend to approach the description of the Ni/Ni_xF_y interlayer in a different fashion, with one or more fluorine atoms chemisorbed on a metallic nickel surface, calculating binding energies as well as evaluating the change in electronic structure. Chemisorption is preceded by physisorption of HF, before cleavage of the H-F bond. Therefore, the reaction profile may also include this intermediate Ni/HF surface.

In this project, the adsorption of HF has been investigated on a Ni(111) surface, some defected variations of it as well as the stepped (211) surface. The adsorption energy of a single HF molecule has been calculated to 26 kJ/mol for the pristine surface. The binding mechanism is typically physisorption and the molecule binds preferably with the H atom to the surface. For fully covered surfaces, we have found that competitive hydrogen bonding between HF molecules prevents adsorption, with a inter-HF binding energy in the order of 40 kJ/mol HF. Moreover, we have applied an electrochemical model for the electrolytic splitting of HF on Ni anodes and cathodes, as is typical for an ECF setup. The model constitutes an explicit HF layer on Ni(111) slabs and suggests the splitting is exothermic already at low cell voltages, which is consistent with experimental findings[7].

We have described the lower index surface cuts of NiF_2 and NiF_3 using the hybrid functional HSE06. With available surface structures, we are able to

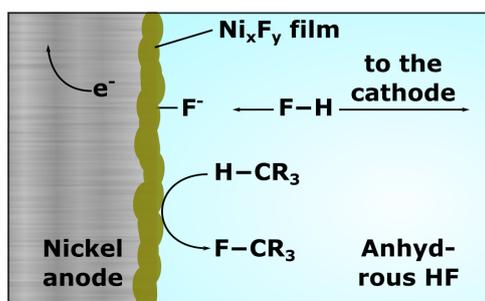


Figure 1: Schematic picture of the Simons process, according to the mechanism proposed by Sartori et al.[3]).

extract the surface energies under an external electrochemical potential. Delicate magnetic ordering and a relatively high degree of electron correlation mainly from the d electrons make these transition metal fluorides notoriously difficult to model even in the bulk structure. Upon studying the bulk phase of CoF_3 , we found that this compound undergoes a Jahn-Teller distortion that leads to a slightly different crystal structure than NiF_3 [8]. Furthermore, we have studied possible bulk phases of Ni_2F_5 using reference crystal structure from compounds of similar stoichiometry. Since this compound may play an important role in the initial oxidation of NiF_2 , we want to perform a global minimum search and obtain a potential energy surface profile for the compound using genetic algorithms.

WWW

<http://userpage.fu-berlin.de/~agpaulus/>

More Information

- [1] A. M. Thayer, *Chem. Eng. News* **15**, 15 (2006).
- [2] J. H. Simons, *J. Electrochem.* **95**, 47 (1949).
- [3] P. Sartori, N. Ignatev, *J. Fluorine Chem.* **87**, 157 (1998).
- [4] E. Skulason, V. Tripkovic, M. E. Björketun, S. Gudmundsdottir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jonsson, J. Nørskov, *J. Phys. Chem.* **114**, 18182 (2010).
- [5] N. Bartlett, R. D. Chambers, A. J. Roche, R. C. H. Spink, L. Chacon, J. M. Whalen, *Chem. Commun.* **1996**, 1049.
- [6] G. Henkelman, H. Jonsson, *J. Chem. Phys.* **113**, 9901 (2000).
- [7] A. Dimitrov, S. Rüdiger, S. Datsenko, N. Ignatev *J. Fluorine Chem.* **50**, 197 (1990).
- [8] S. Mattsson, B. Paulus *J. Comput. Chem.* **40**, 1190 (2019).

Funding

SFB 1349 Fluor-Spezifische Wechselwirkungen