

Modeling electrochemical fluorination using first principles

First principle investigations of electrochemical fluorination on nickel anodes

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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 mechanism presents a couple of challenges to overcome, should it be

properly described by DFT. First, the reaction is non-spontaneous in the absence of an electric voltage, why the electrochemistry needs to be modeled. 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.

We are now interested in the binding of F^- ions on Ni(111) surfaces, pristine and with similar defects. Here, we model the electrochemical steps by the aforementioned Nørskov method. We aim to acquire an understanding of the structure of F^- -adsorbed Ni surfaces at different cell potentials. Our preliminary calculations show that a potential of around 0.5 V is required to initiate the fluorination at a Ni(111) surface, which is comparable to cyclic voltammetry experimental data[6].

In our quest for the nickel and cobalt fluoride sur-

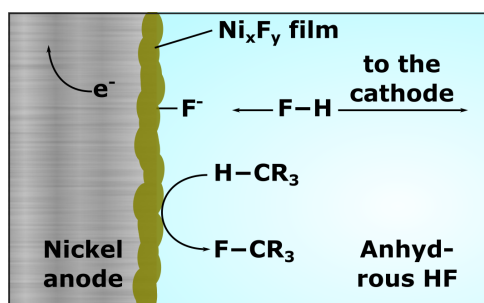


Figure 1: Schematic picture of the Simons process, according to the mechanism proposed by Sartori et al.[3]).

faces, we have already described the lower index surface cuts of NiF_2 . We are currently calculating the NiF_3 surfaces. With available surface structures, we are able to 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 . Furthermore, we have studied possible bulk phases of Ni_2F_5 and found that this compound is less stable than NiF_2 and NiF_3 . These two facts lead us to focus on NiF_2 and NiF_3 surfaces at this stage of the project.

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

More Information

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