Computational analysis of gas-solid interactions in materials for energy storage and conversion - DTU Orbit (14/01/2019)

The extensive use of fossil fuels is harmful to the climate and the general standard of living due to global warming effects and pollution. Thus the rising energy needs in the world caused by an increase in both population and wealth especially in developing countries will have to be met by a renewable energy production. Sustainable energy sources such as solar or wind power are not constant and efficient methods firstly to convert electricity into chemical energy and secondly to store the high energy materials are needed.

In this thesis both issues of conversion and storage are treated. The focus is specifically on the investigation of catalytic materials for electrochemical CO2 fixation into fuels as well as ammonia storage materials, using computational methods relying on density functional theory (DFT) and effective medium theory (EMT) calculations as well as a genetic algorithm. Nanoparticles of binary alloys have previously been shown to be catalytically active for electrochemical CO2 fixation. The stability of the nanoparticles is critical for a catalytic system. We have developed a method to determine the structure and composition of nanoparticles under reactive conditions. This method involves a genetic algorithm for which efficient propagation operators have been implemented and tested on the Cu-Ni alloy system. The algorithm is able to predict the lowest energy structure and composition for the most stable Cu-Ni stoichiometry. At standard conditions in an oxygen atmosphere the particle surface is characterized by regions of Cu atoms and regions of Ni atoms with adsorbed oxygen. Future studies will predict which Cu-Ni stoichiometry will produce a catalytically active particle composition.

Metal ammine chlorides e.g. Mg(NH3)6Cl2 and Sr(NH3)8Cl2, can display high energy storage capacity combined with fast kinetics. We have determined the thermodynamically stable phases of strontium chloride ammines, including the diammine phase, Sr(NH3)2Cl2, that depending on temperature and pressure has a slightly higher or lower stability than the monoammine, explaining why the diammine is only found in certain experiments. We have furthermore determined a stable surface state of ammonia in SrCl2 ammines and identified its implications on the ads- and desorption kinetics. Metal salts often bind ammonia and water molecules in a similar structural coordination. We have studied the competitive exchange and diffusion processes of water and ammonia in magnesium chloride hexammine and hexahydrate as a method for non-thermal release of ammonia. A mixed phase containing both water and ammonia have been shown to be stable in a small region around room temperature.

It is possible to shift the release thermodynamics in metal ammine salts by mixing two or more materials, resulting possibly in a mixed metal ammine salt with superior properties regarding energy content and release temperature. We have used a genetic algorithm to predict several stable mixed metal ammines in model structures with release temperatures in an attractive range for applications in the transport sector.