ENHANCING CATALYTIC ACTIVITY BY ELECTROCHEMICALLY DRIVEN METAL NANOPARTICLE EXSOLUTION

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INTRODUCTION

In heterogeneous catalysis surfaces decorated with uniformly dispersed, catalytically highly active particles are a key requirement for excellent performance. One of the main tasks in catalysis research is the continuous improvement or development of catalytically active materials.

An emerging concept in catalyst design is to selectively and reversibly tune and modify the surface chemistry by electrochemical polarisation. Perovskite-type catalysts raise the opportunity to incorporate guest elements as dopants. Upon electrochemical polarisation these dopants emerge from the oxide lattice to form catalytically active clusters or nanoparticles on the surface (by exsolution). In consequence this leads to a strong modification or enhancement of catalytic selectivity and activity. Electrochemical polarisation offers the possibility to adjust the surface chemistry in response to an external signal in real time (here by the applied voltage).
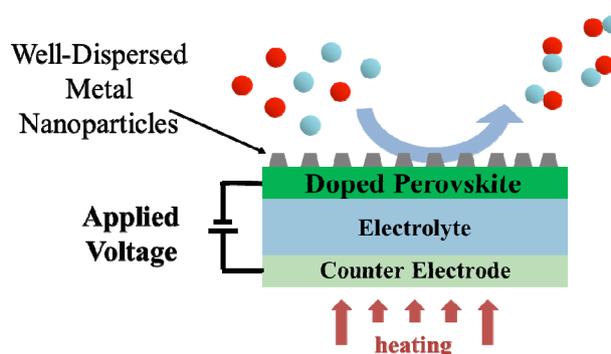

Picture 1: Setup for operando measurements with electrochemical polarization of the surface. Polarization leads to the formation of the metal nanoparticles, which are then enhancing the catalytic activity.

EXPERIMENTS

We present studies for high temperature water splitting[1] and CO_2 electrolysis[2] in a realistic catalytic reaction environment (operando), on different acceptor doped perovskite-type electrodes, and show a direct correlation of surface chemistry with catalytic activity, selectivity and the electrochemical stimulation. This is achieved by a unique combination of surface science, heterogeneous catalysis and electrochemistry.

The experiments were performed at the ISISS beamline of the HZB/BESSY II synchrotron in Berlin with the near-ambient pressure high energy XPS setup (NAPHE-XPS). In this setup XPS and XAS measurements can be performed at elevated pressures (up to 7 mbar) and X-ray energies from 80 to 2000 eV. The setup consists of a high pressure cell with an attached differentially pumped hemispherical analyzer (modified SPECS Phoibos 150) including a 2D delay line detector. For a detailed description of the setup see reference[3].

RESULTS AND DISCUSSION

Exsolution of metallic particles from the perovskite lattice does not affect the kinetics of CO_2 splitting, which is a distinct difference to high temperature H_2O electrolysis were the kinetics were strongly improved. This also contradicts conclusions made from electrochemical CO_2 splitting

measurements with porous perovskite electrodes and supports the importance of the use of model-type electrodes.

The perovskite electrode materials exhibit a rather high coking resilience with carbon deposition only occurring under strongly cathodic polarization. Moreover, the detrimental effects of carbon were completely reversible upon retracting the applied bias without damaging the electrode, which is a very promising result from an application point of view.

REFERENCES

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