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Effect of preparation and oxygen evolution catalysis on CoNiFe oxide electrocatalysts revealed by STEM-EELS

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Background incl. aims
Hydrogen is considered as a competent and green energy carrier that can be obtained by water electrolysis [1]. However, this process is mainly limited by the water oxidation half reaction, the OER (oxygen evolution reaction). Therefore, substantial efforts for this reaction focus on the development of catalysts that are comprised of abundant metals, and which simultaneously fulfil the requirements of high current densities, low overpotential, high mass activity and excellent stability. Here, such a system is presented using CoNiFe oxide in alkaline oxygen evolution. The effect of the synthesis procedure as well as the influence of the catalytic conditions on the material are investigated by STEM coupled with EELS and EDX.

Methods
The catalysts were investigated by a probe corrected JEOL JEM-ARM200F (Schottky emitter) equipped with a Gatan Enfinium ER EELS and a JEOL JED-2300 EDX spectrometer having a silicon drift detector (dry SD60GV). A rather high beam current was applied to keep the acquisition time low. The FWHM of the zero-loss peak (ZLP) was about 1.2 eV and the DualEELS mode was applied. The spectra were recalibrated at each pixel by the position of the ZLP.

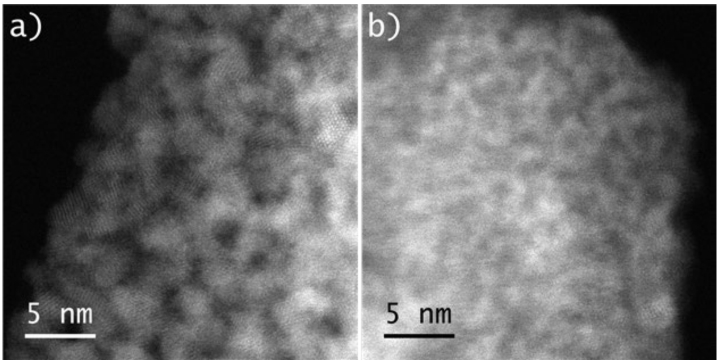
Results
CoNiFe (2:2:1)/M, synthesized under an oxygen-deficient atmosphere (1 vol% air in Ar), shows the best catalytic performance. Synthesis of CoNiFe (2:2:1) under a reductive atmosphere (CoNiFe (2:2:1)/H; 5% H2 in Ar) or oxygen-rich conditions (CoNiFe (2:2:1)/A; air) leads to less active catalysts. While CoNiFe (2:2:1)/M and CoNiFe (2:2:1)/A show a quite uniform distribution of the incorporated metals, CoNiFe (2:2:1)/H shows enrichment of metallic Ni containing nanoparticles on the bulk. More pronounced differences can be observed in the EEL spectra, in particular at the O K edge. Whilst CoNiFe (2:2:1)/A shows a pronounced pre-edge feature at about 528 eV, it is only barely noticeable and slightly shifted to higher energy losses in CoNiFe (2:2:1)/H and CoNiFe (2:2:1)/M. Additionally, CoNiFe (2:2:1)/M exhibits a feature at about 545 eV, which was not present in the other materials. This behaviour is also observed in the spectral regions (L edges) of Co, Ni, and Fe. All M L edge features of CoNiFe (2:2:1)/A ressemble that of oxidized metals M [2-4]. In contrast, CoNiFe (2:2:1)/H and CoNiFe (2:2:1)/M show both, reduced and oxidized states of the contained metals. In CoNiFe (2:2:1)/H, metallic Ni was observed, with Co and Fe remaining oxidic. In addition to metallic Ni, CoNiFe (2:2:1)/M exhibits also partially reduced Co. The incomplete reduction of the metal centers in CoNiFe (2:2:1)/M and CoNiFe (2:2:1)/H is also reflected by the presence of an oxygen signal.

The most active catalyst CoNiFe (2:2:1)/M was also investigated after electrolysis in the absence of nafion. The observed decrease of the ECSA (electrochemically active surface area) was also reflected by a denser appearance of the particles and a decreased size of the crystallites constituting these particles (see graphic). The composition of the material has also changed considerably with a non-uniform distribution of the constituting elements. Some regions lack almost completely Ni and exhibit a reduced contents of iron, leading to a cobalt enriched material. The EEL spectra at the O K edge ressemble those of the fresh catalyst, while the L edges of Co and Fe point towards the presence of these metals in their oxidized forms.

Conclusion

STEM-EELS is a powerful method to investigate changes of electrocatalysts at the nm scale. The different preparation procedures of CoNiFe (2:2:1) yield materials with differently oxidized metals which can be observed by EELS. While CoNiFe (2:2:1)/A exhibits completely oxidized metals, metallic Ni is present in CoNiFe (2:2:1)/H and non-oxidic Ni and Co are present in CoNiFe (2:2:1)/M. After electrolysis in the presence of CoNiFe (2:2:1)/M the signal shape at the O K edge is retained, however, the material is lacking some Ni. STEM-EELS is thus able to detect changes at a very low concentration of the analyte that may escape the eye of bulk analysis methods.

Graphic:



Keywords:

STEM, EELS, OER, oxide, catalysis

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