hpspectroscopy

Advancing electrolysis catalysts with lab-based XANES

Investigation of in situ electroconversion

In a carbon-free future, energy storage systems are becoming ever more crucial for compensating the variable nature of renewable energy sources. Hydrogen production via water electrolysis represents a cornerstone for a potential seasonal and decentralized energy storage. While electrolysis, the electrochemical splitting of water has been known for centuries, its underlying fundamental reactions are still not fully understood. In particular, for the oxygen evolution reaction (OER), the anodic reaction of water electrolyzers, both the exact reaction mechanism and the ideal catalyst still remain to be revealed. The quest for an improved catalyst in terms of activity and stability is important, as the OER currently represents the bottleneck of electrolysis. Inspired by photosynthesis, scientists investigate manganese-based catalysts to boost the OER process.

Even though manganese oxides are promising candidates for enhancing the OER, it turned out that their catalytic activity and stability strongly depends on the preparation process. Most investigated synthesis processes resulted in low activity or deterioration within hours. In contrast, the use of intermetallic precursors, namely $MnGa_4$ resulted in a durable catalyst with superior performance [6]. The $MnGa_4$ precursor undergoes in situ electroconversion and studying this chemical and structural transition in detail is of utmost importance for improving the OER. The oxidation state of both components can be monitored by a combination of X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure spectroscopy (XANES). This combination is particularly powerful, as XPS probes the surface, whereas XANES is bulk-sensitive.

Novel lab-based XANES

The HPS hiXAS is a lab-based XAS solution for both high-resolution XANES and wide-band EXAFS measurements in an energy range extending from 5-12keV. hiXAS uses a highly efficient HAPG crystal in von Hamos configuration. Its non-scanning polychromatic detection permits in-situ measurements and investigations of transitions. Applications in several research areas have already benefitted from this novel tool [1-8].

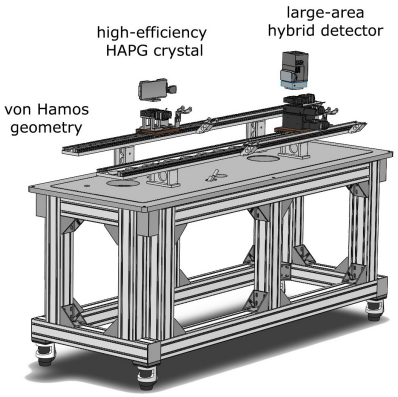

Fig. 1. hiXAS configuration for in-situ recording of spectra with extremely high efficiency

In this study, hiXAS is used to record XANES spectra of Mn and Ga respectively during preparation and after OER cycling. Figure 2 shows the changes of the oxidation states during the process. A comparison to reference spectra indicated that after cycling, Mn is between Mn^{3+} and Mn^{4+} for the entire bulk and Mn^{4+} at the surface (from XPS). Ga vanished from the surface (no longer detected by XPS) and changed from metallic to Ga^{3+} [6].

contact • HP Spectroscopy GmbH
Forggenseestrasse 25
68219 Mannheim
Germany

www • http://www.hp-spectroscopy.com
email • info@hp-spectroscopy.com
tel • +49 176 20949282

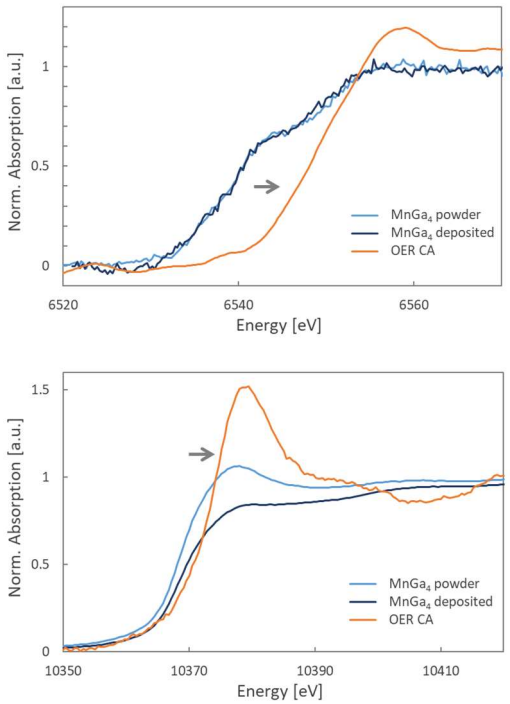

Fig. 2. Top: XANES spectra of Mn after synthesis, after deposition and after OER process. Bottom: Corresponding Ga spectra. The arrows indicate the shift of the absorption edge due to the oxidation. [6]

With XANES as a non-destructive and rapid measurement method, tracking the evolution of a catalyst in-situ or operando becomes a reality. With this method, HPS hiXAS offers researchers continuous and valuable insight into the catalyst oxidation state.

References

1. Schlesiger et al. J. Anal. At. Spectrom., 2015, 34, 1409 – 1415
2. Schlesiger et al. J.Anal. At. Spectrom., 2020, 35, 2298
3. Dimitrakopoulou et al. Faraday Discuss., 2018, 208, 207
4. Bekheet et al. ACS Catal., 2021, 11, 1, 43 – 59
5. Lima Oliveira et al., ACS Sustainable Chem. Eng. 2020, 8, 30, 11171 – 11182
6. Prashanth et al., Angew. Chem. Int. Ed. 2019, 58, 1-7
7. Zhao et al. J. am. Chem. Soc. 2019, 141 (16), 6623 – 6630
8. Le et al. ACS Catal. 2017, 7 (21), 1403 - 1412

contact • HP Spectroscopy GmbH
Forggenseestrasse 25
68219 Mannheim
Germany

www • http://www.hp-spectroscopy.com
email • info@hp-spectroscopy.com
tel • +49 176 20949282