

## Complementary probing the defect and chemical evolution of Co<sub>3</sub>O<sub>4</sub>

Wulyu Jiang<sup>1</sup>, Timon Wagner<sup>2</sup>, Takuma Sato<sup>3</sup>, Brian Wuille Bille<sup>3</sup>, Anna Rabe<sup>4,6</sup>, Martina Rüscher<sup>2</sup>, Joonbaek Jang<sup>2</sup>, Thomas Götsch<sup>1</sup>, Dana Krenz<sup>5</sup>, Sven Reichenberger<sup>5</sup>, Annette Trunschke<sup>1</sup>, Axel Knop-Gericke<sup>1,3</sup>, Olaf Rüdiger<sup>3</sup>, Alexander Schnegg<sup>3</sup>, Janis Timoshenko<sup>2</sup>, Arno Bergmann<sup>2</sup>, Heiko Wende<sup>6</sup>, Stephan Barcikowski<sup>5</sup>, Serena DeBeer<sup>3</sup>, Malte Behrens<sup>4</sup>, Beatriz Roldan Cuenya<sup>2</sup>, Thomas Lunkenbein<sup>1</sup>

<sup>1</sup>Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany

<sup>2</sup>Department of Interface Science, Fritz Haber Institute of the Max Planck Society, Berlin, Germany

<sup>3</sup>Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr 45470, Germany

<sup>4</sup>Institute for Inorganic Chemistry, Christian-Albrechts-Universität zu Kiel, Kiel, Germany

<sup>5</sup>Technical Chemistry I and Center for Nanointegration Duisburg-Essen(CENIDE), University of Duisburg-Essen, Essen, Germany

<sup>6</sup>Faculty of Physics and Center for Nanointegration Duisburg-Essen(CENIDE), University of Duisburg-Essen, Duisburg, Germany

E-Mail presenting author: lunkenbein@fhi-berlin.mpg.de

Cobalt oxides are active in a variety of catalytic applications. In an ideal Co<sub>3</sub>O<sub>4</sub> spinel, all cobalt ions are located in tetrahedral and octahedral sites. In reality, defects account for the typical non-stoichiometry of spinels.<sup>1,2</sup> These defects are believed to play a crucial role in heterogeneous catalysis. Details, on how vacancies and interstitial ions affect the physicochemical properties and the catalytic performance are difficult to obtain as they are difficult to quantify.

Herein, we apply a multi-modal approach that combines results from titration, diffraction, spectroscopy and microscopy experiments to track the evolution of oxygen vacancies in cobalt oxide during the calcination process. In addition, we followed the changes in the geometric and electronic structures in the bulk and at the surface. Results from electrochemical oxygen evolution experiments suggest that the more defective material is more active. The comprehensive structural analysis obtained by the multi-modal line up allows us to establish more realistic defect-activity relationships.

In summary, this work not only provides a deep and comprehensive understanding of material defects but also proves that defect engineering can be an efficient and economical strategy for catalyst design.

[1] Casas-Cabanas, M. *et al. Chem. Mater.* **2009**, *21* (9), 1939–1947. <https://doi.org/10.1021/cm900328g>.

[2] Gawali, S. R. *et al. Sci. Rep.* **2018**, *8* (1), 1–12. <https://doi.org/10.1038/s41598-017-18563-9>