

sized crystalline primary grains within the amorphous network, and their aggregation in nanoparticles, respectively. The amorphous network, which forms within 40 ms, therefore determines the nanocrystalline structure, which forms in the minute range. This template effect not only clarifies why the crystal size is found independent of the nucleation rate, in contradiction with the classical nucleation theory, but also supports the possibility to control the final nanostructure with the amorphous phase.

10:00

Electrochemical Switching of Bulk Properties and Surface Functionality of Perovskite Electrodes ?  
An In-situ XRD and XPS Study

CC.03.6



Authors : Alexander K. Opitz (1), Andreas Nennung (1), Christoph Rameshan (2), Sergey Volkov (3), Vedran Vonk (3), Raffael Rameshan (4,5), Raoul Blume (5,6), Michael Hävecker (5,6), Florian Bertram (7), Axel Knop-Gericke (5), Günther Rupprechter (2), Andreas Stierle (3), Bernhard Klötzer (4), Jürgen Fleig (1)

Affiliations : (1) TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria; (2) TU Wien, Institute of Materials Chemistry, Getreidemarkt 9/165-PC, 1060 Vienna, Austria; (3) Deutsches Elektronen-Synchrotron DESY, Research Group X-ray Physics and Nanoscience, Notkestr. 85, 22607 Hamburg, Germany; (4) University of Innsbruck, Institute of Physical Chemistry, Innrain 80-82, 6020 Innsbruck, Austria; (5) Fritz Haber Institute of the Max Planck Society, Department of Inorganic Chemistry, Faradayweg 4?6, 14195 Berlin, Germany; (6) Catalysis for Energy, Group E-GKAT, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Division Solar Energy Research, Elektronenspeicherring BESSY II, Albert-Einstein-Strasse 15, 12489 Berlin, Germany; (7) Deutsches Elektronen-Synchrotron DESY, Photon Science, Notkestr. 85, 22607 Hamburg, Germany.

Resume : Perovskite-type mixed ionic and electronic conductors are highly attractive functional materials with a wide range of applications in present and future electrochemical devices such as solid oxide fuel and electrolysis cells, gas separation membranes and membrane reactors. In this study, model-composite perovskite electrodes were electrochemically polarized at elevated temperatures in O<sub>2</sub> as well H<sub>2</sub>/H<sub>2</sub>O atmospheres. The polarization induced evolution of surface and bulk properties of the thin film electrodes was monitored in-situ by synchrotron-based XPS and XRD experiments. Electrochemical polarization in O<sub>2</sub> led to XPS binding energy shifts of different cations. These shifts are discussed in the light of defect chemical changes of the electrode, which is supported by XRD results showing chemical lattice expansion. In H<sub>2</sub>/H<sub>2</sub>O applied bias had strong effects on the composition and valence states of near surface cations. On La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3-?</sub> cathodic polarization caused the evolution of a metallic iron species on the electrode surface, accompanied by a strong decrease of the polarization resistance for the water splitting reaction. In XRD experiments the metallic iron species was identified as ?-Fe. After retracting the applied voltage the exsolved iron was immediately re-oxidized and the high water splitting activity disappeared. These results clearly identify the exsolved metallic particles as catalytically active for the electrochemical water splitting reaction and yields new insights in the search for novel electrolysis electrode materials.

10:15

BREAK