

Environmental and In Situ SEM/TEM

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Environmental TEM study of manganite perovskite electro-catalysts for oxygen evolution

C. Jooss¹, S. Raabe¹, D. Mierwaldt¹, J. Ciston², S. Yazdi³, T. Kasama³, M. Beleggia³, J.B. Wagner³, T.W. Hansen³, Y. Zhu⁴, P. Blöchl⁵

¹University of Goettingen, Institute of Materials Physics, Goettingen, Germany

²Lawrence Berkeley National Laboratory, National Center for Electron Microscopy, Berkeley, California, United States

³Technical University of Denmark, Center for Electron Nanoscopy, Lyngby, Denmark

⁴Brookhaven National Laboratory, Department of Condensed Matter Physics, Upton, NY, United States

⁵Technical University of Clausthal, Institute of Theoretical Physics, Clausthal, Germany

jooss@ump.gwdg.de

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In-situ studies of catalysts are of high interest since they offer the opportunity to study their atomic and electronic structure in the active state. We present an environmental transmission electron microscopy (ETEM) study of O₂ evolution catalysis during H₂O splitting based on Pr-doped CaMnO₃ (PCMO) perovskite electro-catalysts. These systems offer the opportunity for fundamental studies of the role of variable Mn valence state, surface structure and defect chemistry for multi-step charge transfer.

ETEM studies of electro-catalytic water splitting are a challenge, since electro-catalytic activity must be separated from beam effects. In addition, gas phase reactions of H₂O and intermediates at the catalyst surface are difficult to be observed. Here, we show that PCMO fundamentally changes surface morphology and atomic surface structure in contact with water vapor. Oxygen evolution induced by electron beam stimulation can be monitored by mass spectrometry. In addition, oxygen evolution can be visualized by oxidation of silane which reacts with oxygen and thus forms solid SiO_{2-x} at catalytically active surfaces [1]. In order to develop an understanding of the beam induced effects in the catalyst in the presence of gas, we performed a series of control experiments: ETM studies of catalytic activity in water vapor are combined with in-situ X-ray absorption spectroscopy (XANES) and ex-situ cyclic voltammetry studies. Electron energy-loss spectroscopy (EELS) as well as the in-situ XANES reveal that the Mn valence is decreased in the active state. Our assumption that oxygen evolution is driven by a positive potential which is induced in the catalyst by inelastic scattering of high energy electrons and subsequent secondary electron emission is supported by off-axis electron holography. First steps in electro-chemical control of the catalyst are performed using a Nanofactory STM-TEM holder and applying an electric bias to the TEM sample. Careful TEM analysis of samples measured by ex-situ cyclic voltammetry and in-situ bias-controlled ETM experiments allow us to distinguish between self-formation of the active state during oxygen evolution and corrosion processes at the Pr_{1-x}Ca_xMnO₃-H₂O interface. Based on results from density functional theory (DFT) calculations, we can correlate trends in O₂ evolution activity and defect chemistry in the active state to doping induced changes of the electronic band structure in A-site doped manganites.

1. S. Raabe, D. Mierwaldt, J. Ciston, M. Uijtewaal, H. Stein, J. Hoffmann, Y. Zhu, P. Blöchl, and Ch. Jooss, In-situ electrochemical electron microscopy study of oxygen evolution activity of doped manganite perovskites, *Adv. Funct. Mater.* 22 (2012) 3378–3388, DOI: 10.1002/adfm.201103173

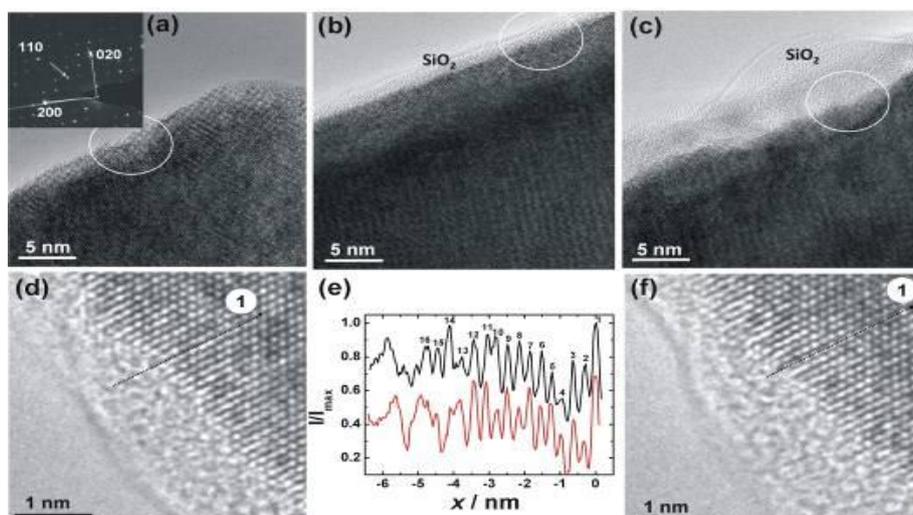


Figure 1. ETEM study of crystalline PCMO with $x=0.32$ during electron and water exposure. (a) High-resolution TEM image acquired in high vacuum showing the pristine state of a grain at [001] zone axis. The same section as in (a) is shown during an ETEM experiment in water vapor ($p_{\text{H}_2\text{O}} = 0.04$ mbar), where the growth of an amorphous SiO_{2-x} layer indicates oxygen evolution activity of the edge (b) 20 s and (c) 70 s after start of the electron beam stimulation. The circle is a marker for a specific edge location. (d) and (f) High-resolution TEM images of a grain at [201] zone axis after 300 s and 310 s of electron beam exposure in water vapor and resulting SiO_x coverage. (e) Intensity modulation along the same line depicted in (d) and (f). The first atomic column of this line is labeled as “1”.

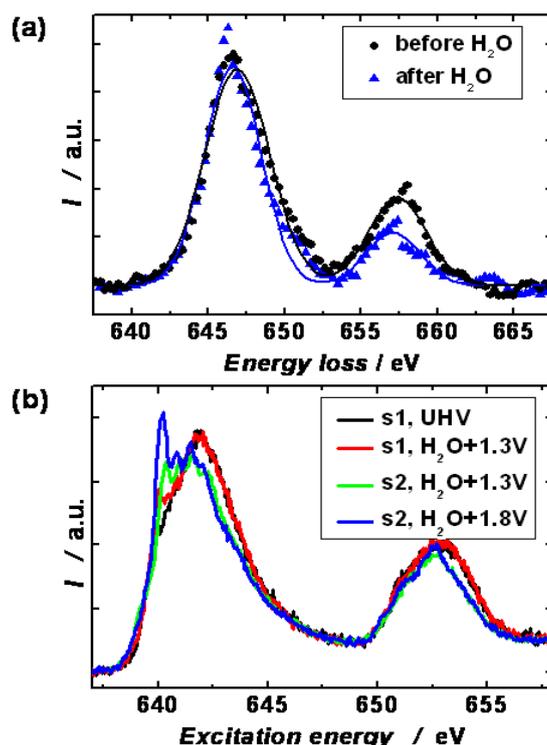


Figure 2: Change of the Mn L-edges in the active state of PCMO with $x=0.32$ revealed by ETEM (a) and in-situ XANES (b) experiments. (a) Core loss electron energy-loss spectra after Hartee-Slater background subtraction before and after electrocatalytic O_2 evolution. Both spectra are acquired in high vacuum mode before switching to and after switching back from ETEM operation mode and stimulating the sample in 0.013 mbar H_2O vapor with 10^4 $\text{e}/\text{\AA}^2\text{s}$. The L_3/L_2 ratio increases from 2.5 to 4.8. (b) In-situ XANES study of two PCMO films s1 and s2 with $x = 0.32$ in UHV and in contact with H_2O vapor at different positive bias. The increase of intensity at the L_3 edges at about 640.3 eV indicates an increasing fraction of Mn^{2+} .