

Operando X-ray absorption of La(Ni,Fe)O₃ thin films in the electrocatalytic oxygen evolution reaction

Reports: The electricity-driven anodic materials in the liquid often suffered from surface structure revolution leading to much complex identification. Herein, we use an operando X-ray absorption spectroscopy (XAS, **Swiss Light Source**) to track the dynamics of the electronic structure in the electrocatalytic oxygen evolution reaction. The active materials are 3 to 10 nm thin films of La(Ni,Fe)O₃, grown epitaxially on 100 nm conductive La_{0.67}Sr_{0.33}MnO₃ layers with pulsed laser deposition (PLD). The perovskite layers are supported on monolayer Ca₂Nb₃O₁₀ nanosheet-buffered 100 nm SiN_x membranes. The La(Ni,Fe)O₃ films are in contact with 1.0 M KOH solution and the operando Fe K-edge and Ni K-edge XAS spectra were measured from the SiN_x backside using total fluorescence yield under different potentials. The XAS spectra show significant spectra changes that (1) the metal valencies remain constant and (2) an increased covalence of transition metal 4p and oxygen 2p states, where the modified covalency correlates with the activity descriptions (in preparation, unpublished).

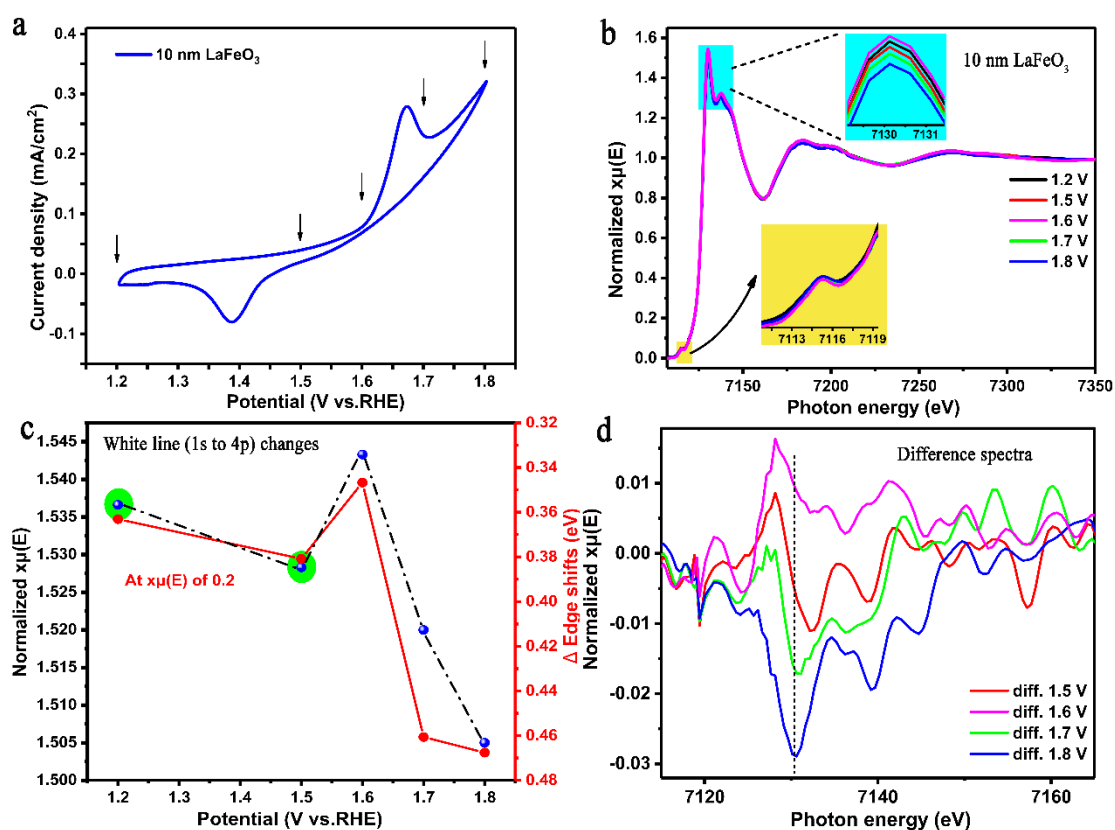


Figure 1. (a) The CV measurements of 10 nm LaFeO₃ with a scan rate of 10 mV·s⁻¹ in 1.0 M KOH solution. (b) Related operando Fe K-edges XAS recorded at 1.2 V, 1.5 V, 1.6 V, 1.7 V, and 1.8 V vs.

RHE, insert white line regions and enlarged pre-edges of 1s to 3d quadrupole transition). (c) Corresponding white lines (the highest intensity) and edge shifts (7122 eV + Δ) at an intensity of 0.2 respectively as a function of potentials. (d) The difference spectra using a 1.2 V XAS spectra as a standard.

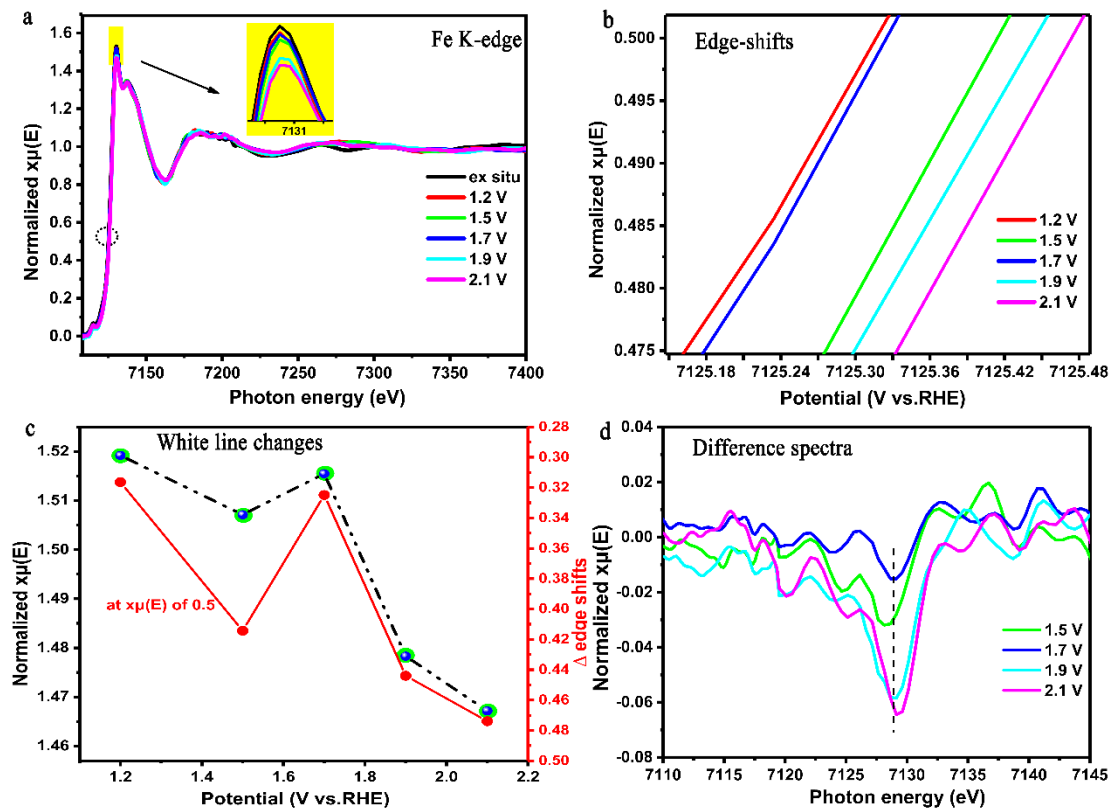


Figure 2. (a) The operando Fe K-edge XANES of 3.1 nm-3.2 nm LaNiO₃/LaFeO₃ and ex-situ without liquid. (b) The edge shifts near the sharp region of first derivation at 1s to 4p. (c) The white line and edge shifts (7125 eV + Δ) at an intensity of 0.5 respectively as a function of potentials. (d) The related difference spectra by subtracting an absorption spectroscopy at 1.2 V.