Operando X-ray characterization of complex oxide electrocatalyst surfaces and interfaces

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Earth-abundant, active, selective and stable electrocatalysts are important for our transition to defossilization of the chemical industry, sector coupling, and sustainable energy. The catalyst surface is known to transform at the interface with the electrolyte, especially under operation conditions. Yet the properties of the transformed catalyst surface, not the as-prepared state, give rise to observed metrics like activity and stability. This complicates predictive electrocatalyst materials design.

We employ single crystalline surfaces obtained from epitaxial thin films to investigate atomic-level structure-property relations in the electrochemical oxygen evolution reaction. These serve as a well-defined starting point for in situ and operando characterization of interfaces and surface transformations during the reaction. Throughout the talk, I will refer to examples from perovskite oxide thin films and heterostructures, including nickelates, cobaltates and manganates.[1–4] We selectively tune the surface and subsurface cationic composition in epitaxial growth. Examples include so-called high entropy oxides (HEO) such as $LaCr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}O_{3-\delta}$, where high electrocatalytic activity is observed and believed to result from synergistic interplay in the complex composition.[5]

In situ and operando X-ray photoemission and X-ray absorption studies reveal the catalysts' electronic structure, surface composition, and phase transformations during operation, as well as the binding of intermediates like oxygen and hydroxide species. These insights into the true active surface phase are a pathway for the rational, predictive design of next-generation energy materials.

References

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