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In situ and operando Characterization of Model Perovskite Oxide Electrocatalysts

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Electrocatalytic generation of chemical fuels such as hydrogen enables storing intermittent renewable energies, and perovskite oxides are among the most attractive candidate materials to catalyze the kinetically limiting half reaction, the oxygen evolution reaction (OER). OER activity is typically correlated to electronic and atomic structure parameters. But the catalyst surface –i.e. where the reaction happens –changes during the reaction. To design next-generation electrocatalysts, a detailed operando understanding of the relationships between catalytic activity, stability and atomic-level surface properties during the reaction is required.

In my talk I will address two essential ingredients to achieve this next-level understanding: Firstly, epitaxial thin films are a direct route for single crystalline model electrocatalysts that can be fabricated with atomically-tailored surface composition. These offer the ideal platform to derive structure-property-function relationships, track the evolution of the surface properties with applied potential and enable direct comparison to the surfaces investigated in density functional theory. Secondly, I will discuss application and challenges of surface-sensitive operando characterization in a liquid medium, with specific attention to atomically-defined thin film model electrode surfaces. Information from the outermost surface of a catalyst can be obtained through a standing-wave approach^{1,2} or extraction of a surface-only signal from careful thickness-dependent studies.³

The key example will be LaNiO₃ thin films, which are atomically flat both before and after application as electrocatalysts for the OER during water electrolysis. We selectively tuned the surface cationic composition in epitaxial growth. The Ni-termination is approximately twice as active for the OER as the La-termination.¹ Using a suite of ex situ, in situ and operando spectroscopy tools, we found that the Ni-rich surface undergoes a surface transformation towards a catalytically active Ni hydroxide-type surface.¹ If LaNiO₃ surfaces are exposed to the CO₂-containing atmospheres, however, surface carbonate groups decrease the activity as evidenced by APXPS.⁴

Our work thus demonstrates tunability of surface transformation pathways by modifying a single atomic layer at the surface. It also highlights the need of and summarizes pathways for the exploration of the three-step relationship between as-prepared surface, transformation under applied potential, and electrocatalytic activity.

References

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if "Other", please specify:

I apply for a travel grant

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