

Pulsed Laser Deposition for Energy Materials

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A fundamental understanding of material properties and reactions in energy materials can often be achieved through advanced large-facility techniques, such as those available at synchrotrons or neutron sources. These techniques provide unique insights but often require well-defined samples with controlled properties, including crystallinity, surface roughness, and interface quality. Such requirements are frequently met by using thin films. To this end, we employ Pulsed Laser Deposition (PLD) to fabricate thin films, enabling the application of complementary methods ranging from neutron reflectometry (NR) to grazing incidence X-ray absorption spectroscopy (GIXAS).

One material system we study involves Li-containing materials for Li-ion batteries, with the ultimate goal of developing a thin-film battery entirely fabricated by PLD. A major challenge in this approach is identifying a suitable solid electrolyte that retains its properties in thin-film form. Many oxide electrolytes, such as LLZO ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) or LLTO ($\text{Li}_{3x}\text{La}_{(2/3-x)}\text{TiO}_3$), do not meet these criteria. Additionally, it is essential to identify oxide-based electrode materials (anode and cathode) that are compatible with the solid electrolyte, particularly in terms of deposition conditions and interfacial properties.

Another key area of our work focuses on oxynitrides, which are used as photoanodes for photo-electrochemical (PEC) water splitting. Despite their promise, this material class suffers from rapid activity decay during the initial electrochemical cycles and a gradual long-term decline. The long-term decay is likely linked to material degradation, such as nitrogen loss. However, the fast decay remains poorly understood, hindering the development of strategies to address it.

By utilizing thin films as model systems, we studied the mechanisms behind the fast decay. Using neutron reflectometry (NR), we observed a surface modification within a 3 nm region, manifested as a density change. Concurrently, X-ray absorption spectroscopy (XAS) revealed alterations in the oxidation states of constituent elements. Specifically, the A cation exhibited changes in oxidation state, while the B cation (e.g., in LaTiOxNy), traditionally considered the active site, underwent localized disordering. This surface modification compromises water-splitting activity. However, we identified a co-catalyst capable of suppressing these modifications.

Our investigations uncovered critical steps in the PEC water-splitting mechanism. During surface modification, the formation of NO_x competes with the desired oxygen evolution reaction (OER). Without highly defined, high-quality PLD-fabricated thin films, it would not have been possible to leverage large-facility techniques to uncover and mitigate the origins of activity decay in oxynitrides for water splitting.