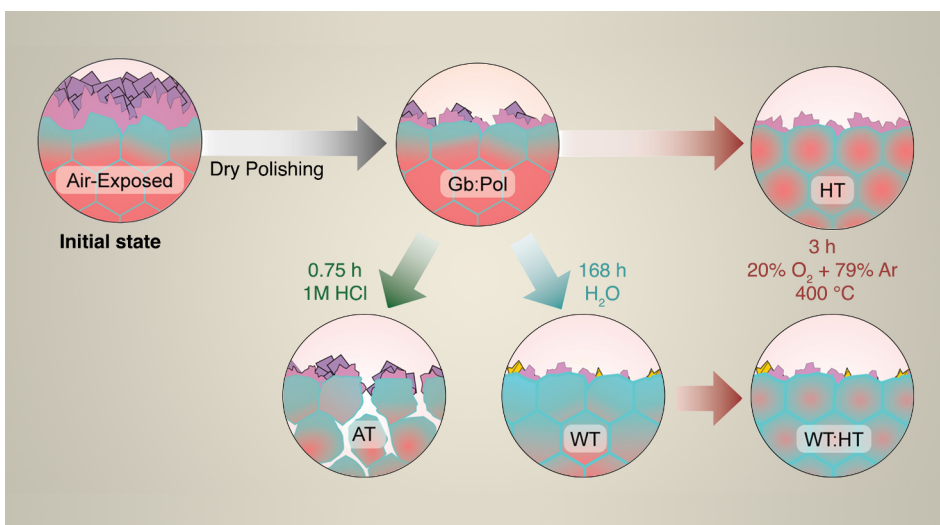


# Studying Interfacial Effects in Solid-Electrolyte Batteries



Illustrations of some of the surface treatments applied to a solid-state battery-electrolyte material (LLZO) as part of this study: glovebox polishing (Gb:Pol), heat treatment (HT), acid treatment (AT), water treatment (WT), and water treatment + heat treatment (WT:HT). Proton concentration (the result of  $H^+$  displacing  $Li^+$ ) is indicated by the color gradient, from low (orange) to high (blue). Pink and purple indicate surface contaminants.

## A solid prospect for better batteries

Global efforts to electrify transportation and provide grid-level energy storage have driven demand for new battery technologies with improved safety, power density, and energy density. Ceramic solid electrolytes potentially offer significant advantages compared to the traditional liquid electrolytes used in lithium-ion batteries, including lower flammability and greater compatibility with high-energy electrode materials such as lithium metal. Among solid-electrolyte contenders, tantalum-doped lithium lanthanum zirconium oxide (LLZO) has garnered significant attention as a separator material because of its high bulk ionic conductivity and minimal chemical reactivity with lithium metal.

However, LLZO performance is limited by reactions that produce surface contaminants. Understanding the mechanisms behind these reactions is crucial for improving material processing. In this work, researchers used ambient-pressure x-ray photoelectron spectroscopy (APXPS) as part of a systematic investigation of the impacts of electrochemical reactions and contamination. The results will inform the design of safer and more-efficient batteries for electric vehicles or renewable energy storage.

### Facing the interfacial challenges

It is well known that, in the presence of water vapor in air, LLZO undergoes  $Li^+/H^+$  exchange, where protons ( $H^+$ ) can take up lithium-ion ( $Li^+$ ) sites without modifying the cubic crystal structure. This results in

## Scientific Achievement

At the Advanced Light Source (ALS), an ambient-pressure probe of a solid electrolyte revealed how surface electrochemical mechanisms lead to poor electrolyte performance and battery failure.

## Significance and Impact

The results can help scientists engineer better coatings and interfaces, which are essential for building safer and better-performing batteries, particularly for use in vehicles.

the formation of surface contaminants such as  $LiOH$  and  $Li_2CO_3$  that contribute to poor interfacial contact and the constriction of current.

Numerous studies have explored different aspects of the surface contamination mechanisms on LLZO along with various processing techniques aimed at improving surface properties. However, most studies have focused on critical current density (CCD) tests, which provide limited mechanistic insight, or impedance analyses, with limited rationale behind their interpretation.

In this study, the researchers utilized a variety of surface-treatment processes on LLZO pellets to selectively induce proton exchange and contamination reactions in LLZO. The resulting bulk and surface

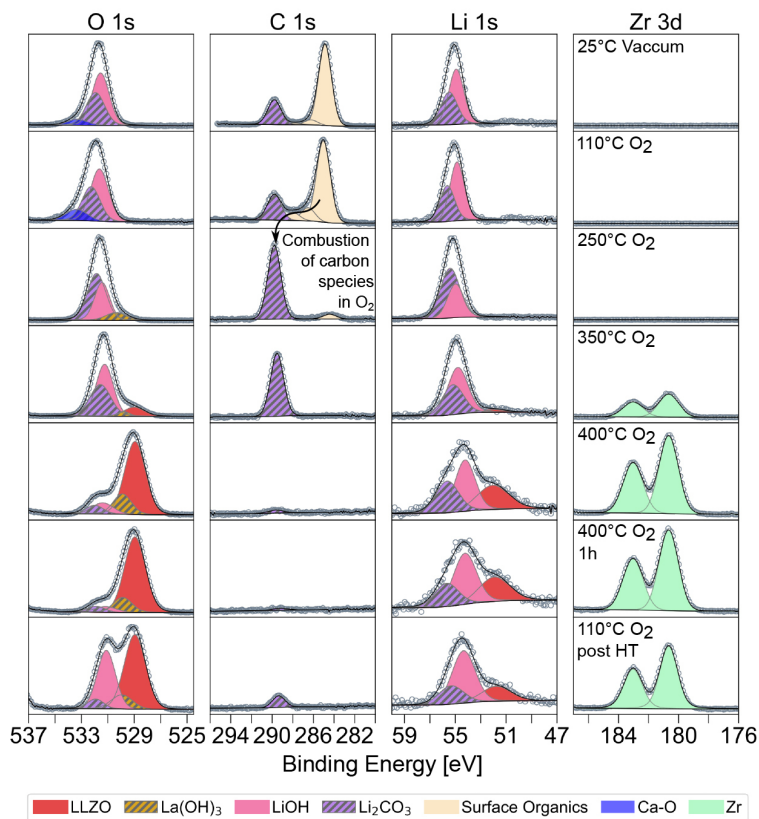
chemistry was systematically characterized and correlated to changes in electrochemical properties.

## ALS studies at ambient pressure

To observe the evolution of chemical species near the LLZO surface as temperature increases, ambient-pressure x-ray photoelectron spectroscopy (APXPS) was performed at ALS Beamline 9.3.2. The ability to tune the gas environment and temperature during measurement was crucial, as it allowed the researchers to optimize conditions (pressure, temperature, time) for removing surface contaminants. Also, the ability to vary the probe depth via beam energy was also essential for chemical speciation.

The results demonstrated that maintaining a contaminant-free LLZO surface is likely only possible above temperatures of 350–400 °C or under ultrahigh vacuum. Although LLZO's susceptibility to moisture and LiOH formation was well known, the extent of this sensitivity was surprising, possibly indicating a fundamental limitation of the material. The persistent presence of ionically resistive contaminants such as LiOH also supports the study's electrochemistry and modeling results, which suggest that the constriction resistance commonly observed at the lithium/electrolyte interface is not solely due to voids but also to ionically resistive surface layers.

Overall, this work advances our understanding of surface contamination reactions on LLZO and establishes correlative insights into its electrochemical performance that are also broadly applicable to other solid electrolyte systems.



Select APXPS data for air-exposed LLZO samples heated from room temperature to 400 °C in 500 mTorr O<sub>2</sub>. The main contaminants observed at 25 °C in vacuum are LiOH (pink) and Li<sub>2</sub>CO<sub>3</sub> (purple). The combustion of surface organics at T ≥ 200 °C produces CO<sub>2</sub>, which causes significant Li<sub>2</sub>CO<sub>3</sub> formation. Further heating leads to the near-complete removal of LiOH and Li<sub>2</sub>CO<sub>3</sub>, with a notable decrease in contaminants from 350 to 400 °C; this decrease is accompanied by the appearance of photoemission peaks attributed to LLZO (red) and Zr (green). However, the contaminant-free LLZO surface is not preserved after cooling—significant quantities of LiOH and trace amounts of Li<sub>2</sub>CO<sub>3</sub> are observed upon returning to 110 °C.

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