Laser Sintering of LLZO Films for Solid-State Batteries

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Motivation & Scientific Concept

The **LASIBAT project** aims at developing high-performing solid-state batteries with laser-sintered LLZO electrolytes. Laser sintering [1,2] utilizes high-energy photon radiation to melt the particle surfaces in order to consolidate the material. The process, illustrated in **Figure 1**, is fast (seconds) and highly localized (micrometers), which makes it attractive for **in-line manufacturing of LLZO electrolyte films directly onto heat-sensitive electrode materials**. For blue lasers, tuning the LLZO laser absorption properties, e.g. by using additives like CuO [3], is crucial for achieving sufficient sintering of the LLZO film.

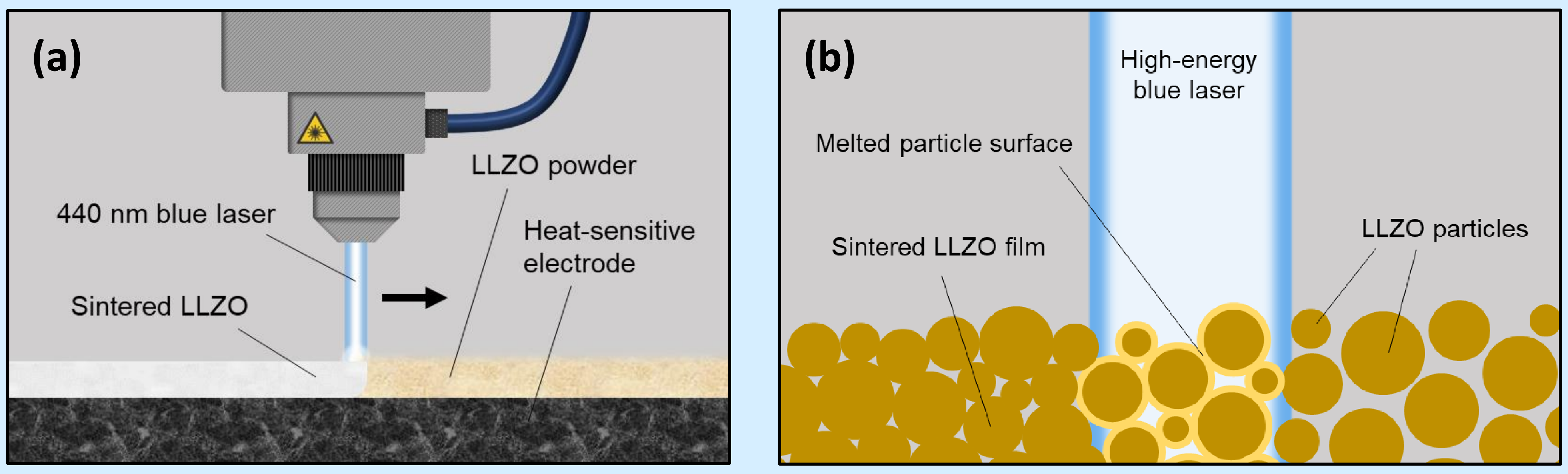
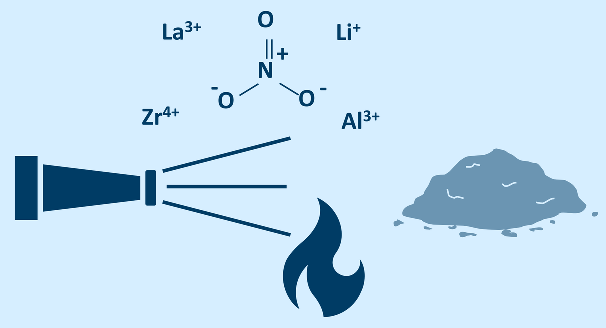


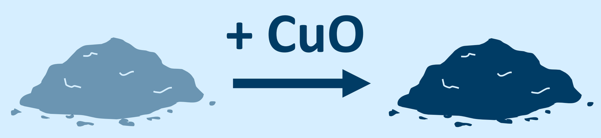
Figure 1: (a) The LASIBAT project concept; laser sintering of LLZO directly on the electrode. (b) Assumed working principle: Melting of grain interfaces while keeping core crystallinity.

Methods

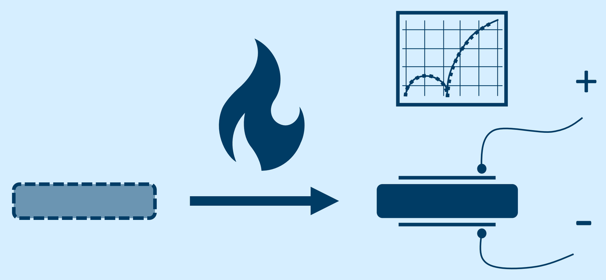
1 Spray pyrolysis of Al-doped LLZO powder



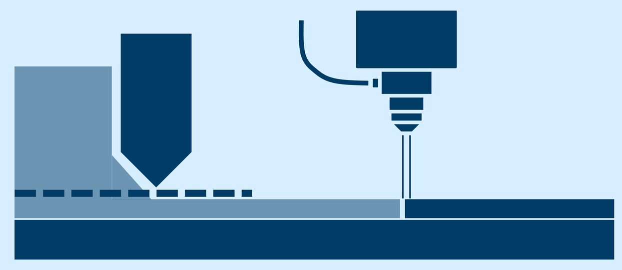
2 Mixing LLZO and CuO absorption additive



3 Sintering of bulk pellets for electrical analysis



4 Laser sintering of screen-printed LLZO films



Results

UV-Vis light absorption measurements of LLZO-CuO powder blends (**Figure 2**) demonstrate that CuO increases the absorption from 4% in pure LLZO to 31%, 41% and 49% for 1, 2 and 3 wt% CuO, respectively. The abscence of CuO reflections at 36° and 39° in the XRD patterns (**Figure 3**) and the homogeneous distribution of Cu in the EDX mapping (**Figure 4**) suggest that CuO enters the LLZO structure during sintering. LLZO pellets containing 1 wt% CuO have higher ionic conductivity at room temperature (1.29 mS/cm) and lower activation energy for Li migration (0.38 eV) compared to samples with 0 wt% (0.41 mS/cm, 0.39 eV), 2 wt% (0.54 mS/cm, 0.43 eV) and 3 wt% (1.03 mS/cm, 0.38 eV) CuO (**Figure 5**). SEM images of laser-sintered LLZO films (**Figure 6**) show that 1 wt% CuO improves densification and widens the window of operation during laser sintering compared to pure LLZO.

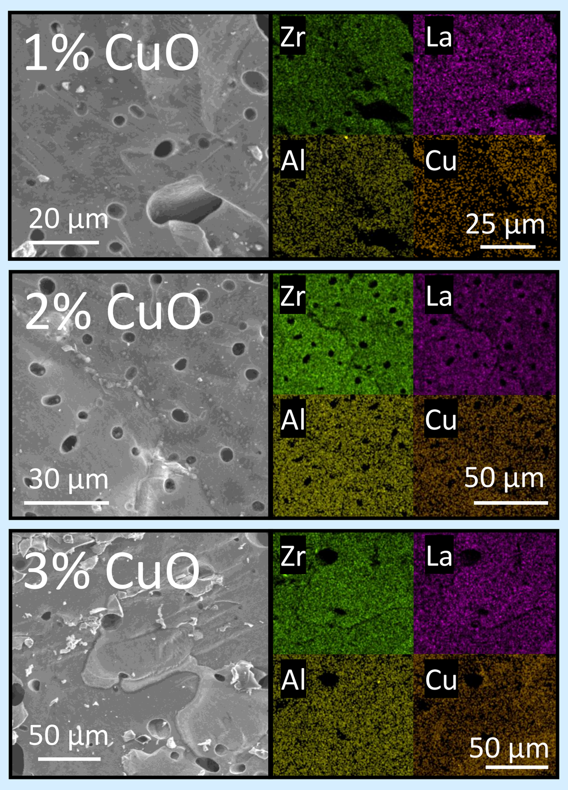


Figure 4: SEM and EDX images of LLZO-CuO pellets.

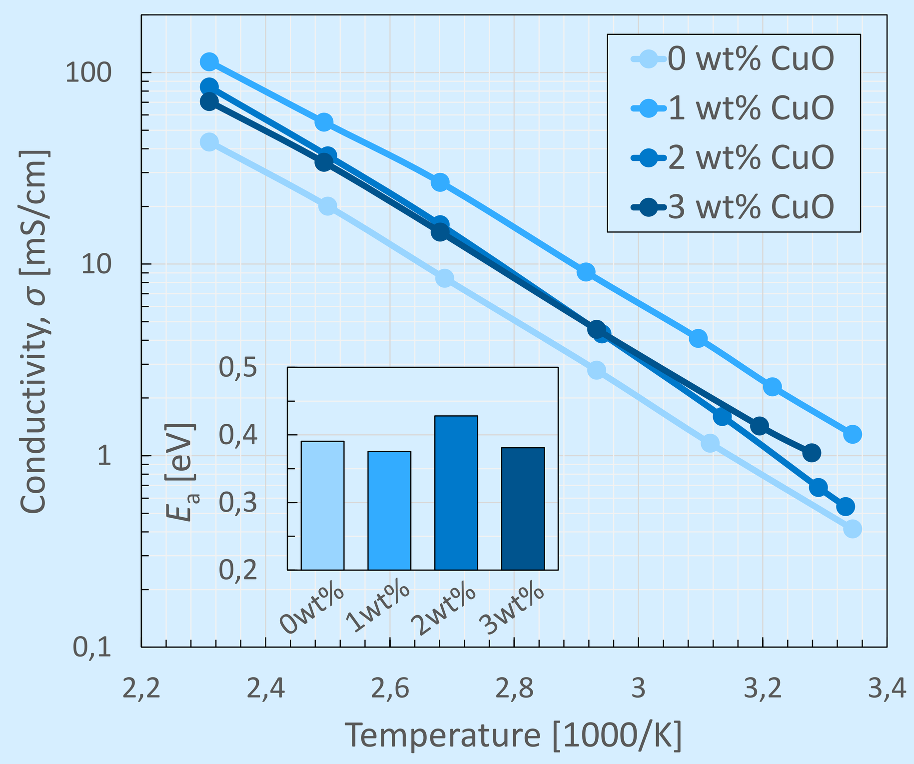


Figure 5: Conductivity from 25 to 160 °C and activation energy of LLZO-CuO pellets.

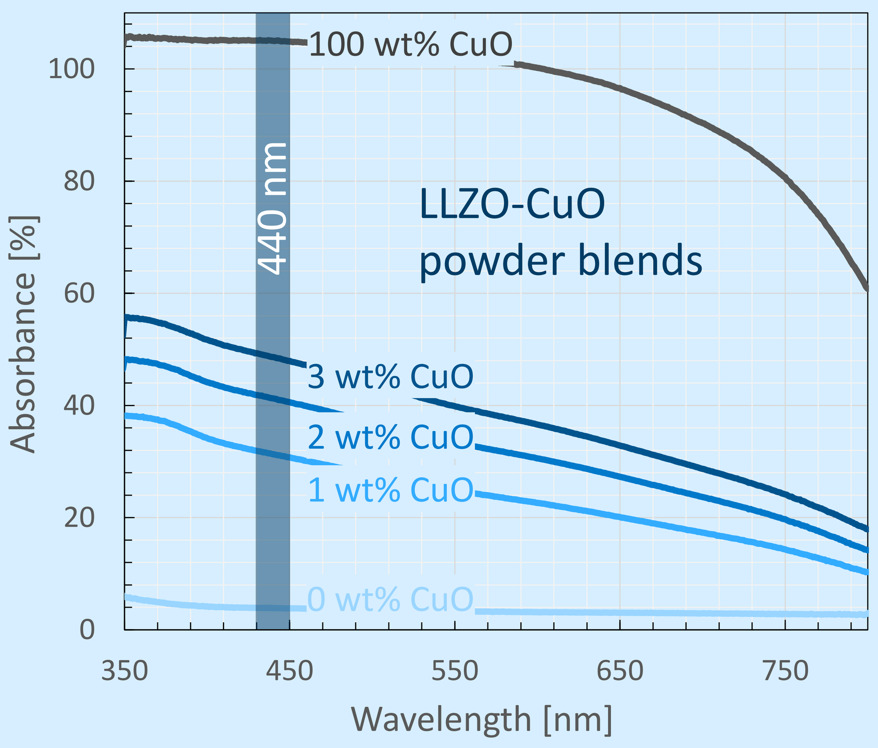


Figure 2: UV-Vis light absorption spectra of LLZO-CuO powder blends.

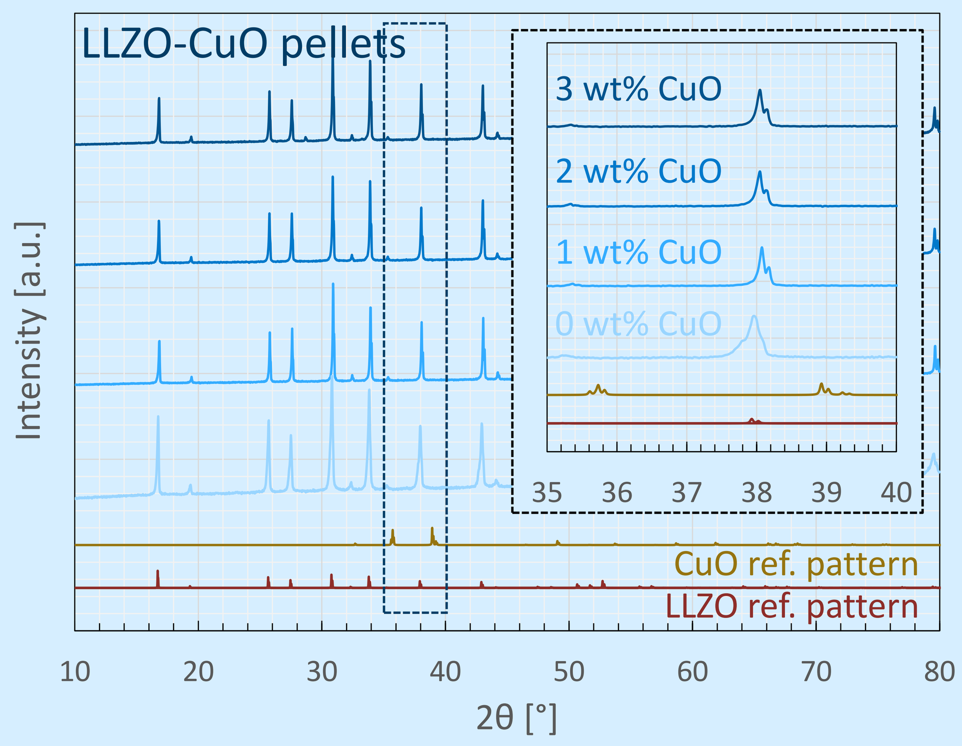


Figure 3: XRD patterns of sintered LLZO with varying amounts of CuO.

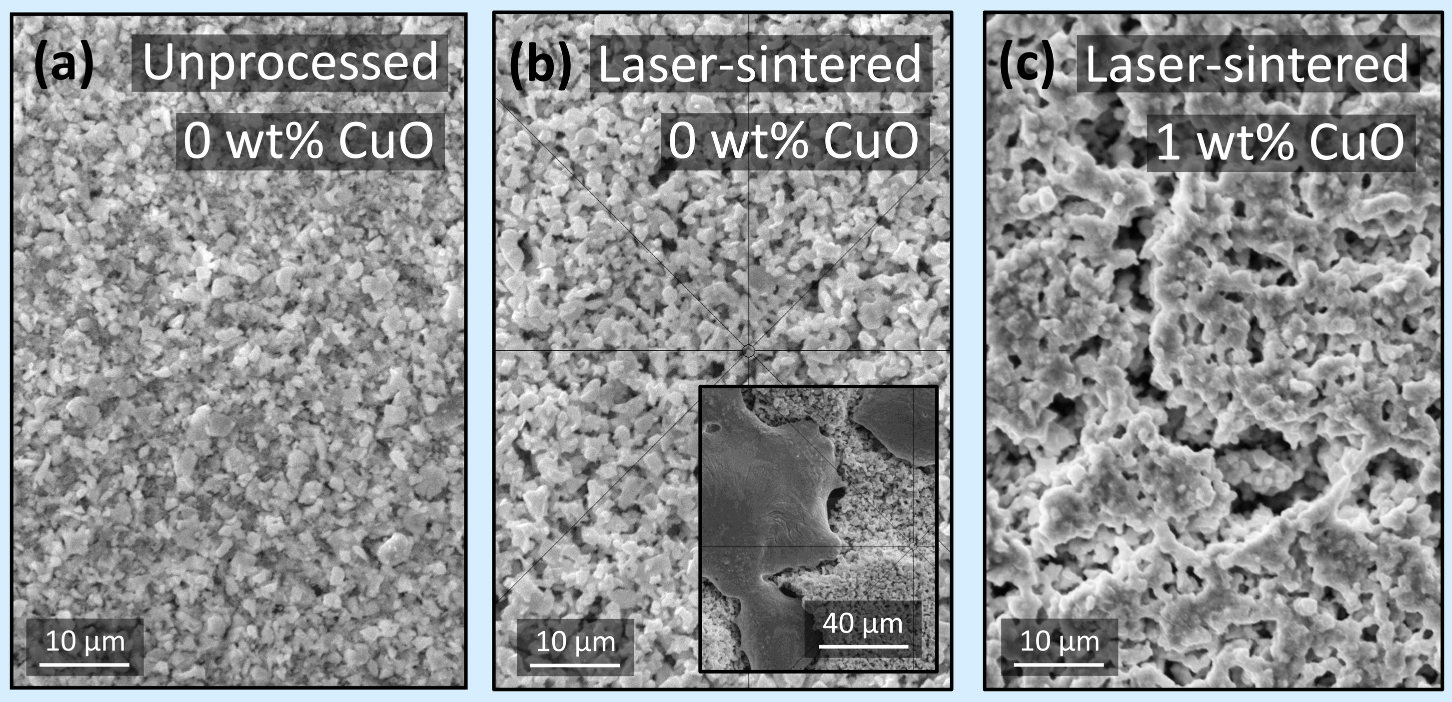


Figure 6: SEM images of screen-printed LLZO films. (a) Unprocessed film, and laser-sintered LLZO films with (b) 0 wt% CuO and (c) 1 wt% CuO.

Conclusions & Outlook

- Laser sintering holds the potential for precise and efficient in-line manufacturing of LLZO electrolytes for solid-state batteries.
- For sintering with blue laser radiation at a wavelength of 440 nm, additives like CuO are necessary to increase the photon absorption of LLZO to improve sinterability.
- Adding 1 wt% CuO absorption additive to LLZO increases the UV-Vis photon absorption at 440 nm, improves the densification of LLZO films during laser sintering, increases the Li ion conductivity, and lowers the activation energy for Li migration.
- Integration of laser sintered LLZO-CuO electrolytes with battery electrodes for cell testing is being pursued.

Acknowledgements

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