Supporting Information

Design of Triple and Quadruple Phase Boundaries and Chemistries for Environmental SO_2 Electrochemical Sensing

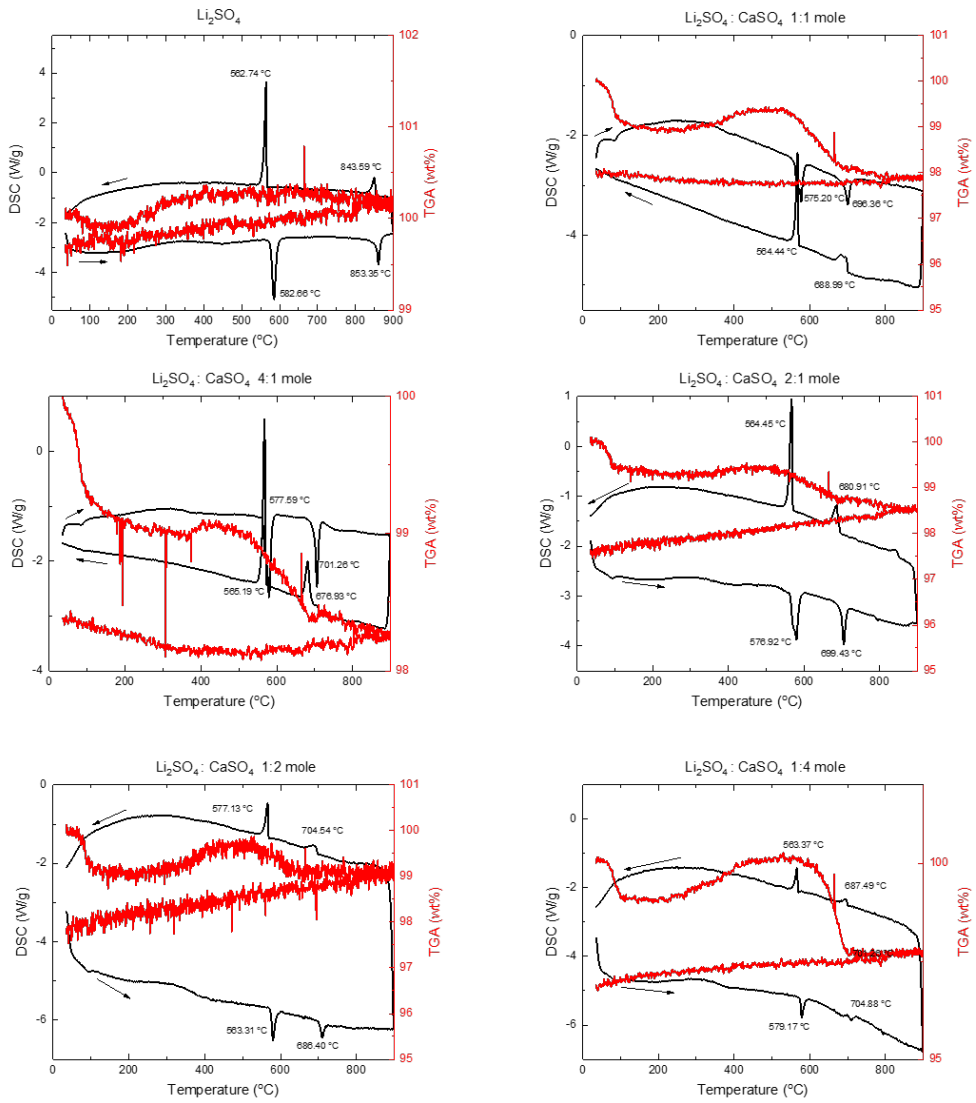
Moran Balaish[a] and Jennifer L.M. Rupp[a,b,*]

[a]Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

[b]Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, US

[*]Corresponding author email: jrupp@mit.edu

The melting points of Li_2SO_4 and $CaSO_4$ mixtures containing 0, 20, 33, 50, 67, 80, and 100 mol% $CaSO_4$ were determined using DSC (**Figure S1**). The results confirmed that the addition of $CaSO_4$ (20–80 mol%) lowered the melting point of the mixture by ~150 °C from 853 °C (100% Li_2SO_4) to ~700 °C, correlating with the reported Li_2SO_4–$CaSO_4$ phase diagram.[17] The results also indicated that a firing temperature of 750 °C was required to ensure complete melting of the Li_2SO_4–$CaSO_4$ sulfate mixture and improve the adhesion between the sensing-electrode layer and the solid electrolyte. Our *in-situ* XRD investigation[12] confirmed that LLZO exhibited excellent stability properties and could support the processing temperature required, i.e. 750 °C, to achieve the complete melting of the solid electrolyte. Thus, the auxiliary electrode chemical composition of Li_2SO_4–$CaSO_4$ in a mole ratio of 1:1 was selected, which was brushed directly on the surface of the LLZO solid-electrolyte pellet, dried, and heated to 750 °C to secure improved adhesion between the dense sensing electrode and solid electrolyte (**Figure 1c**).



Mole ratio of Li_2SO_4:$CaSO_4$	1:0	1:1	4:1	2:1	1:2	4:1
$T_{Orth \rightarrow cubic}$ [˚C]	582	575	577	577	577	576
T_m [˚C]	853	696	701	699	705	705

Figure S1. Melting temperature of the sensing electrode as a function of its composition determined via DSC/TGA analysis of different mole ratios of Li_2SO_4:$CaSO_4$. The measurement was conducted under synthetic air from room temperature to 900 °C, held for 5 min, and cooled back to room temperature at a ramp rate of 10 °C/min for both the heating and cooling steps. The melting temperatures are also summarized in the table above.