Supporting information for: Ion dynamics and CO_2 absorption properties of Nb, Ta and Y-doped Li_2ZrO_3 studied by solid-state NMR, thermogravimetry and first-principles calculations

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SEM and EDX analysis

Scanning electron microscopy (SEM) and EDX experiments were performed on the Nb and Y doped samples to determine whether the dopants were incorporated into the Li_2ZrO_3. Representative images of the two samples are shown in Figure S1 and Figure S2. For the purposes of identifying the phases present, the most reliable value is the Zr:dopant atomic ratio, due to the better sensitivity of EDX to heavier elements. As it can be seen in the EDX spectra for both samples in Figure S3, the ratio is approximately consistent with a 5% doping on the Zr site. The Ta doped sample was unable to be analysed due to overlap of the Ta emission line with other elements present in the sample, but due to the similar chemical and structural behaviour of Nb and Ta we expect it to also be doped uniformly into the Li_2ZrO_3 phase.

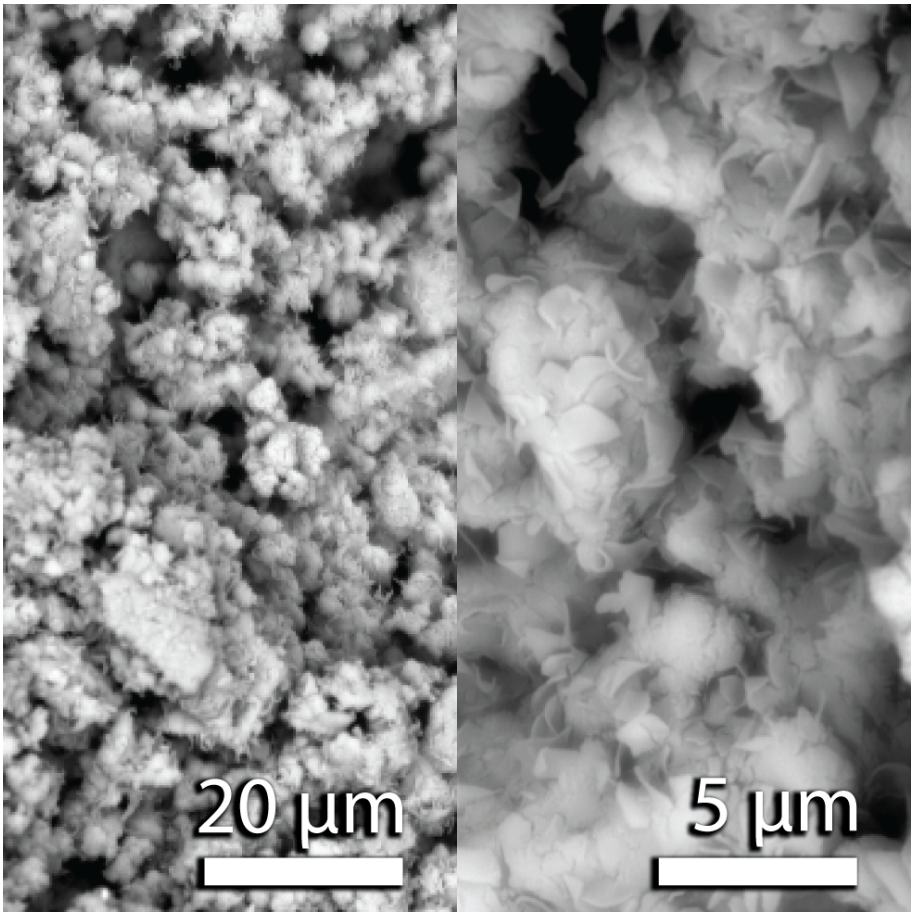

Figure S1: Backscattered electron micrographs of $Li_{1.95}Zr_{0.95}Nb_{0.05}O_3$ prepared in this study demonstrate the powder is formed of curled plates ~ 50 nm thick by $\sim 1\ \mu$m along a side.

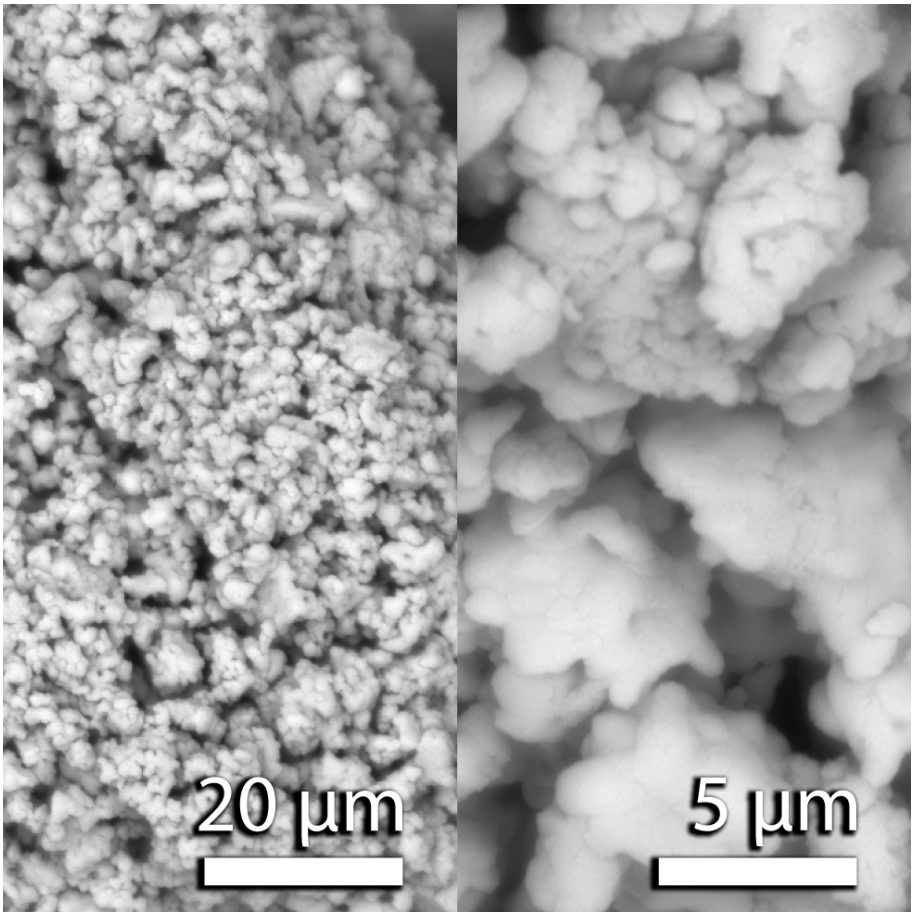

Figure S2: Backscattered electron micrographs of $Li_{2.05}Zr_{0.95}Y_{0.05}O_3$ prepared in this study demonstrate the powder is formed of agglomerated particles $> 1\,\mu$m in diameter.

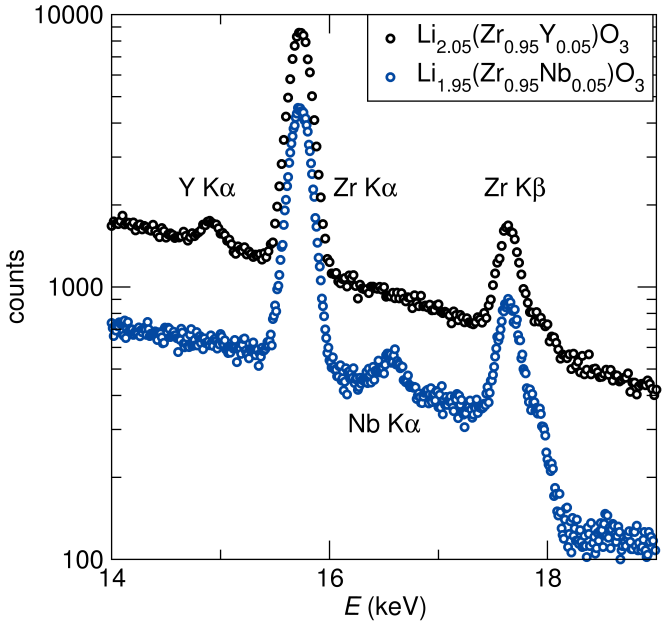

Figure S3: The presence of Y or Nb fluorescence lines in EDX spectra confirm Y and Nb are incorporated into Li_2ZrO_3. Spectra collected from multiple particles across a specimen indicate Y and Nb are homogeneously distributed throughout the material.

2×2×2 Ta-doped supercells

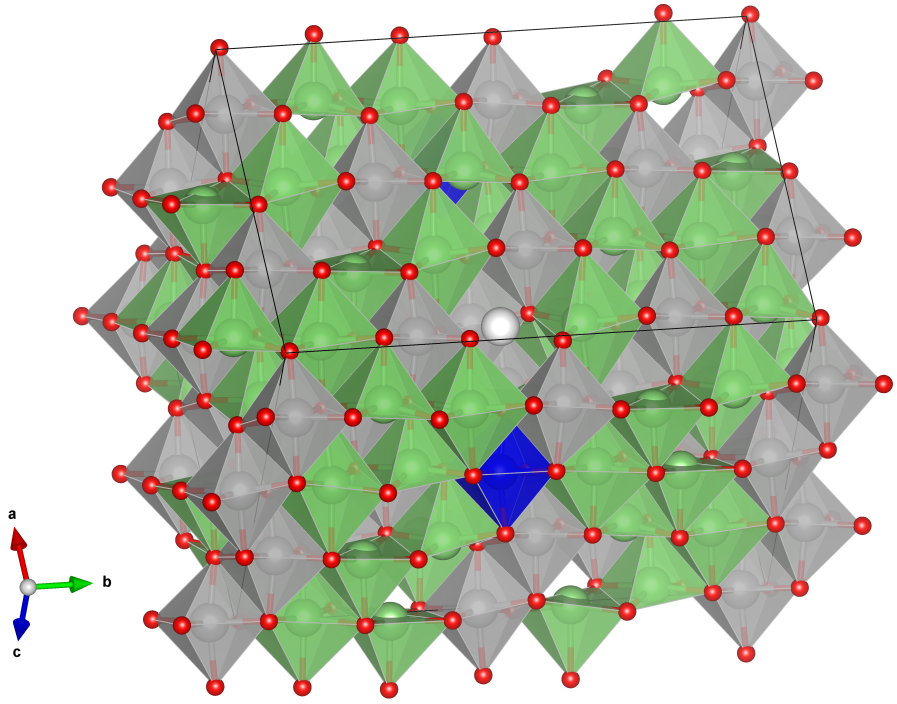

Figure S4: The lowest energy doping configurations computed Ta in a 2×2×2 supercell with composition $Li_{56}Zr_{31}TaO_{96}$. The coordination polyhedra of Li, Zr and Ta are shown in green, grey and blue respectively, with O atoms in red. The vacant Li site is shown as a white sphere.

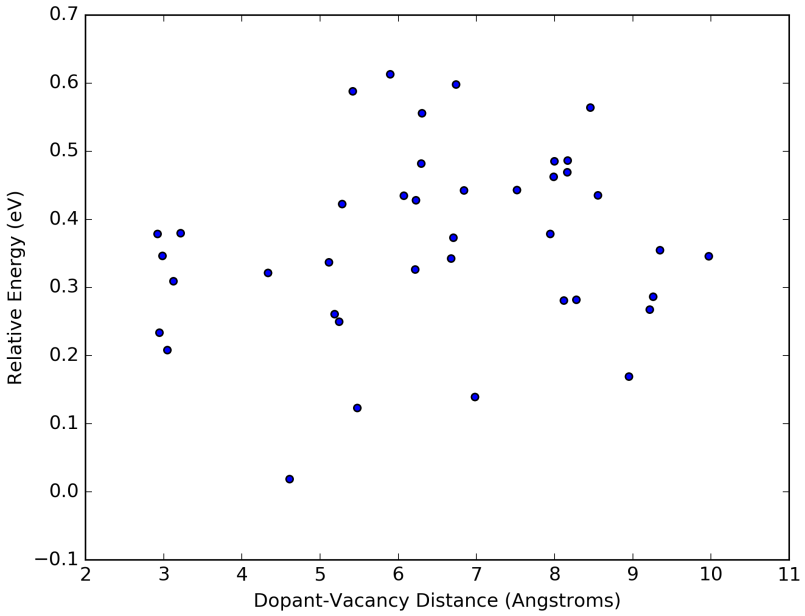

Figure S5: Energy of each DFT-optimsed configration for a $2\times2\times2$ supercell of Li_2ZrO_3 with one dopant Ta atom, plotted against the vacancy-dopant distance. No correlation is seen between the two parameters across the configurations calculated.

Lattice parameters determined from Rietveld refinements

Table S1: Rietveld-refined lattice parameters of $Li_{2-x}Zr_{1-x}Nb_xO_3$, $Li_{2-x}Zr_{1-x}Ta_xO_3$ and $Li_{2+x}Zr_{1-x}Y_xO_3$.

Dopant	x	a (Å)	b (Å)	c (Å)	β (°)
Nb	0.00	5.4307(2)	9.0254(3)	5.4247(2)	112.769(2)
	0.05	5.4308(2)	9.0001(2)	5.4205(2)	112.968(3)
	0.10	5.4334(1)	9.0005(3)	5.4184(2)	112.964(2)
	0.25	5.4260(2)	8.9933(4)	5.4125(2)	112.925(3)
Ta	0.00	5.4307(2)	9.0254(3)	5.4247(2)	112.769(2)
	0.05	5.4369(2)	9.0049(2)	5.4263(2)	113.008(3)
	0.10	5.4355(1)	8.9921(3)	5.4219(2)	113.073(2)
	0.25	5.4222(2)	8.9659(4)	5.3966(2)	113.031(3)
Y	0.00	5.4307(2)	9.0254(3)	5.4247(2)	112.769(2)
	0.05	5.4376(2)	9.0349(2)	5.4326(2)	112.841(3)
	0.10	5.4310(1)	9.0274(3)	5.4329(2)	112.846(2)

VT ^{7}Li NMR spectra of undoped Li_2ZrO_3

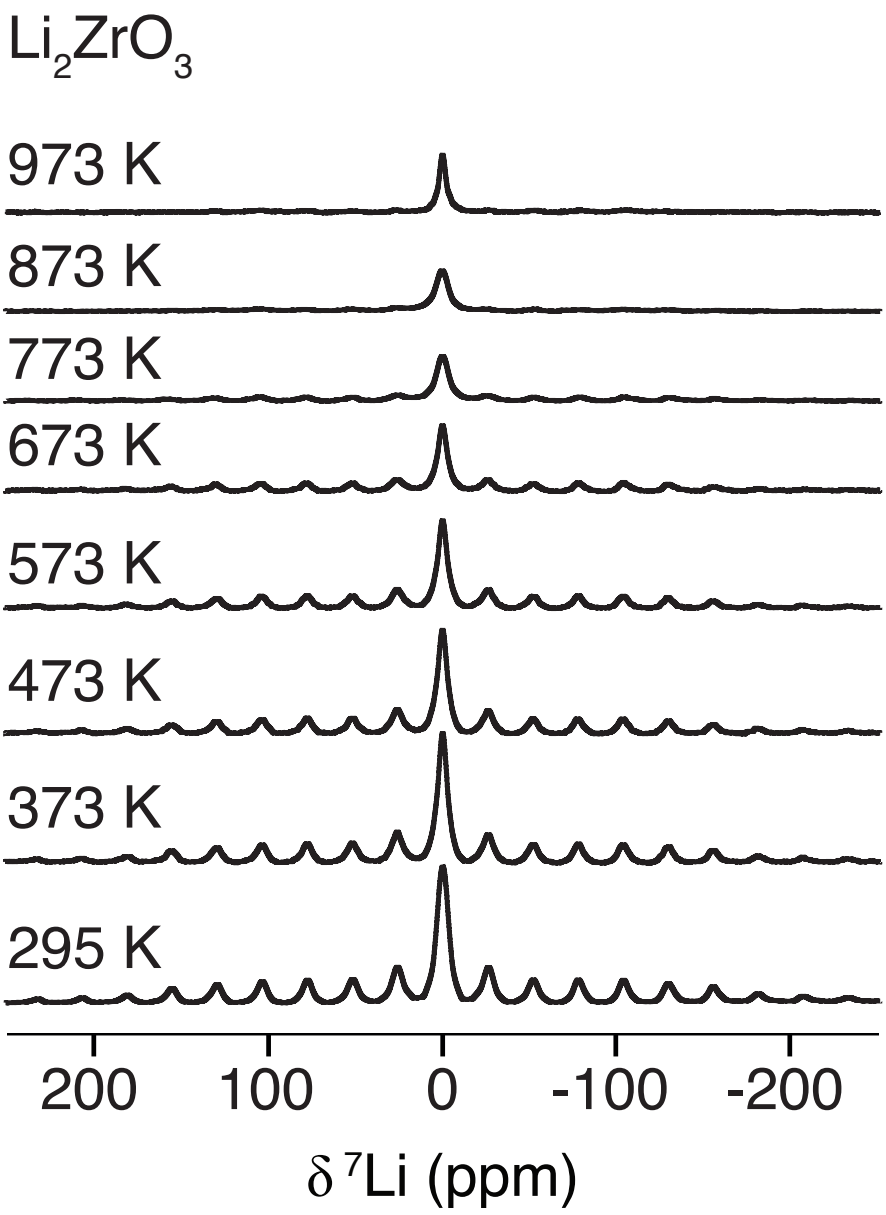

Figure S6: ^{7}Li MAS NMR spectra for lzo measured from 295–973 K. The spectra were normalised between samples to the intensity at 295 K. Like the doped samples, with increasing temperature a narrowing of the central transition linewidth and a broadening and subsequent narrowing of the satellite transition linewidths is observed, although at a higher temperature than the doped samples.