

Supplemental Information for
Enhanced ion transport in Li₂O and Li₂S films

Simon Lorget, Kai Narita, Robert Usiskin,* and Joachim Maier

Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany

* Email: r.usiskin@fkf.mpg.de

Experimental details

Li₂O and Li₂S films decompose readily when exposed to humidity, and the resulting LiOH is clearly visible in XRD patterns.¹⁸ In this work, Li₂O and Li₂S materials were handled strictly in an argon-filled glovebox (Mbraun, H₂O and O₂ levels below 0.1 ppm), under vacuum below 10⁻⁴ mbar, or under flowing bottled gas (argon and/or O₂, Westfalen, 99.999%) using leak-checked gas lines and chambers. Thin films of Li₂O and Li₂S were grown by RF magnetron sputtering using elemental targets (Li for Li₂O; Li and S₈ for Li₂S) or ceramic targets (Li₂O). The preparation steps were described previously.¹⁸ The sputter parameters used here are given in Table I of that work. Films were grown at 150 °C (Li₂O) or 290 °C (Li₂S) on single crystal substrates of Al₂O₃ (0001), MgO (100), LiF (111), or MgF₂ (001) (Crystec GmbH, 10 × 10 × 0.5 mm, one side polished). The substrates were used as received, except in a few cases, the substrates were first rinsed with acetone and then isopropanol. X-ray diffraction patterns were acquired under vacuum using the second setup described in ref. ¹⁸ Raman spectra (HORIBA, iHR 550 spectrometer, BXFM microscope) were acquired in the same setup using a confocal geometry (532 nm, 10 mW). Scanning electron microscopy and focused ion beam milling (Zeiss Merlin and Crossbeam) were used to measure film thicknesses from cross sections. Images of the film surfaces were acquired to estimate the grain sizes. As a caveat, the SEM images do not have sufficient resolution to distinguish if grain sizes smaller than 20 nm are present, especially below the film surface, and the Scherrer estimate obtained by XRD inherently tends to fall above the mode of a particle size distribution.⁴⁵ Thus, these data do not exclude the presence of sub-20 nm grains or amorphous material, especially in the as-grown films near the substrate.

To look for unintended impurities and dopants, a Li₂O film was characterized by time of flight - secondary ion mass spectrometry (TOF.SIMS 5, Iontof). Trace F, Cu, and Ca were detected with estimated concentrations of 0.05 at% each, with an uncertainty of roughly one order of magnitude. Sulfur was also detected, suggesting a small degree of cross-contamination in some Li₂O films. This effect was judged to be inconsequential, in part because some Li₂O films showing enhanced conductivity were obtained before an elemental sulfur target was ever introduced into the sputter chamber. Other elements showed low concentrations, typically well below 0.05 at%; the precise estimates varied somewhat depending on the measurement mode.

For transport measurements, most films were contacted by 100–200 nm thick ruthenium electrodes (Lesker 99.95%, 0.05 cm spacing, 7.5 cm interdigitated length) applied by DC sputtering (Emitech K575X) through a shadow mask. The measurements in Figure S3 used a simpler geometry (0.5 cm spacing, 0.8 cm length, not interdigitated). The measurements in Figure S4 used Li⁺-selective electrodes consisting of Li foil (Alfa Aesar, 99.9%) pressed against a solid Li⁺ electrolyte (Ohara, Li-Al-Ti-Si-P-G-O composition). The foil-electrolyte contact was sufficient for the purposes here, despite being not chemically stable. After applying electrodes, all samples were pressed against Pt wires, installed in a quartz chamber inside a tube furnace, and heated under 50 standard cubic centimeters per minute (~10 cm/s) argon flow to various temperatures in the range 25 – 340 °C as measured by a thermocouple placed adjacent to the substrate. The typical dwell to allow equilibration after each temperature change was 1 h. Impedance spectroscopy (Novocontrol Alpha-A) was performed over the range 10⁶ to 10⁻² Hz. The extracted resistance R was converted to conductance and conductivity by $G = 1/R$ and $\sigma = L/(RA)$, where L is the electrode spacing and A is the cross-sectional area (which equals film thickness * electrode length). The effective capacitance (calculated from $C_{\text{eff}} = Q^n R^{1-n}$, where Q and n are the magnitude and exponent of the constant phase element) was 5 pF in all spectra, consistent with stray capacitance from the substrate. Above about 180 °C, a second arc began to appear in the spectra at low frequencies; this arc was considered to be evidence of ion-blocking behavior at the electrodes and was otherwise neglected.

Supplemental figures

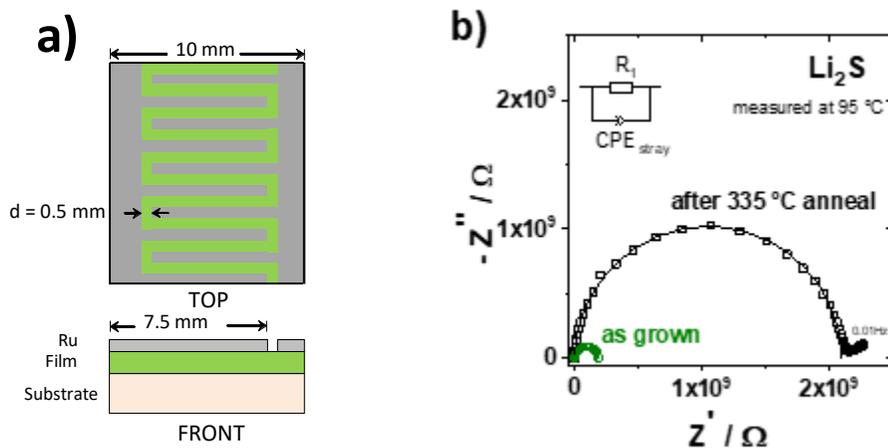


Figure S1. (a) Schematic of the interdigitated electrode geometry used for impedance measurements. (b) Typical impedance spectra acquired as grown and after annealing.

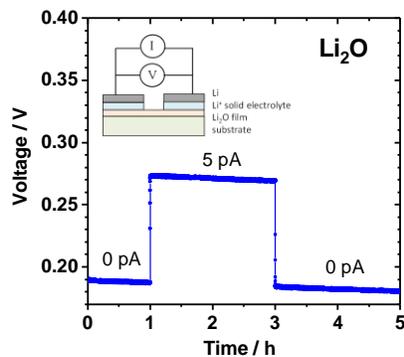


Figure S2. DC measurement at 144 °C of an as-grown Li_2O film using an applied current of 5 pA. The data were acquired using Li^+ -selective electrodes in the configuration shown in the inset.

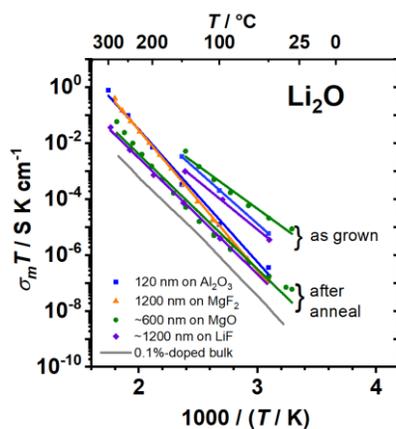


Figure S3. Conductivity behavior of Li_2O films grown on various substrates from a ceramic Li_2O target. The activation energy of $\sigma_m T$ is 0.6–0.7 as grown and increases to 0.8–1.0 after annealing. Comparison data from a bulk sample doped with 0.1 mol% LiF are also shown.⁸

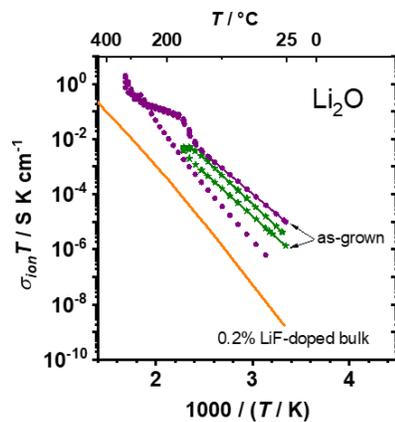


Figure S4. Conductivity of two Li_2O films grown on Al_2O_3 at $150\text{ }^\circ\text{C}$, including the transient (non-stationary) data obtained while heating above $150\text{ }^\circ\text{C}$. Both samples show an increase in conductivity at $165\text{ }^\circ\text{C}$.

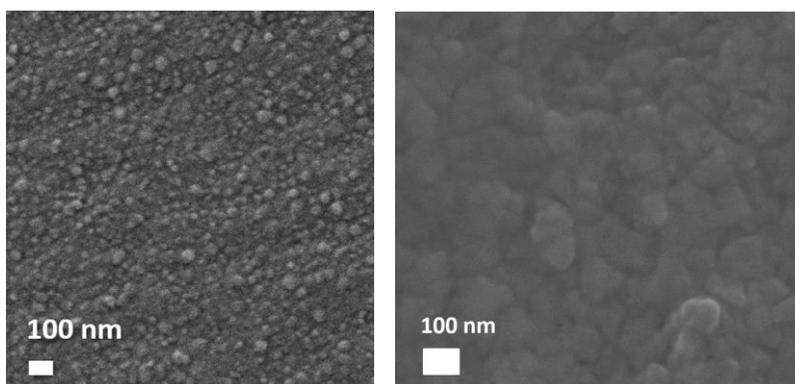


Figure S5. Typical SEM images of the as-grown film surfaces: (left) Li_2O , (right) Li_2S .

Table S1. Ionic conductivity at 25 °C of bulk samples of the individual compounds typically found in lithium battery SEI layers. All values were measured by impedance spectroscopy. When necessary, extrapolations from measurements starting at 100–300 °C were used, as discussed in the notes. Adapted with permission from ref. ⁴⁷.

Material	$\log_{10}(\sigma_{\text{ion}}(25\text{ °C}) / \text{S cm}^{-1})$	Type of crystal	Reference	Notes
Li alkyl carbonates (C1-C8)	<-12	poly	Schafzahl et. al., Chem. Mater., 30, 3338 (2018)	Values are from Figure 4 and the text. Abstract incorrectly gives 10^{-9} S cm ⁻¹ for Li methyl carbonate.
Li ethylene monocarbonate (LEMC)	-5.2	poly	Wang et. al., Nat. Chem., 11, 789 (2019)	
amorphous Li ethylene dicarbonate (LEDC)	<-9	amorph	Wang et. al., Nat. Chem., 11, 789 (2019)	
Li methyl carbonate (LMC)	<-9	poly	Wang et. al., Nat. Chem., 11, 789 (2019)	
Li ₃ N c-axis	-5 to -5.4	single	Rabenau, Solid State Ionics, 6, 277 (1982)	
Li ₃ N ab-plane, poly	-3 to -3.2	single	Rabenau, Solid State Ionics, 6, 277 (1982)	Originally reported in Alpen et. al., Appl. Phys. Lett., 30, 621 (1977). Agrees with Boukamp & Huggins, Mater. Res. Bull. 13, 23 (1978).
Li ₃ N ab-plane	-5 to -2.2	single	Lapp et.al., Solid State Ionics, 11(2), 97 (1983)	doped with Mg, Cu, Al, or H.
Li ₃ N ab-plane	-3.4 to -2.5	single	Hooper et al., Mat. Res. Bull., 14, 1617 (1979)	H-doped
Li ₃ N c-axis	-7.7 to -6.7	single	Hooper et al., Mat. Res. Bull., 14, 1617 (1979)	H-doped
Li ₃ P	-3.3	poly	Nazri, Solid State Ionics, 34, 97 (1989)	
Li ₂ O	-12.1 to -11.3	poly	Lorger, J. Electrochem. Soc., 166, 10, A2215 (2019)	Various dopings

Li ₂ S	-14 to -10	single + poly	Lorger, Adv. Funct. Mater., 1807688 (2018)	Various dopings
LiOH	-13	poly	Johnson, Mat. Res. Bull., 12, 577 (1977)	Extrapolated from 110 °C. Same data were given in Biefeld 1979 J. Electrochem. Soc. The data are shown in Figure 4 as an upper bound because they could be from H ⁺ conduction instead of Li ⁺ conduction.
LiF	-14	single	Lehfeldt, Z. Physik, 717 (1933)	Extrapolated from 250 °C.
LiF	-17 to -15	single	Geschwind, J. Phys. Chem. Solids, 30, 6, 1631 (1969)	Extrapolated from 45 °C. Lower values for “undoped”, higher values for Ca doping. Undoped data were also published in Geschwind, J. Am. Ceram. Soc., 51, 9, 539 (1968).
LiF	-16.7 to -14.5	single	Stoebe, J. Phys. Chem. Solids, 28, 1357-1382 (1967)	Higher values were from undoped LiF; lower values were from LiF doped with LiOH.
LiCl	-12 to -10	single	Sharon, J Solid State Chem., 40, 20-27 (1981)	Undoped or doped with Sr or Ca. Extrapolated from 275 °C, roughly accounting for association.
Li ₂ CO ₃	-18 to -14	poly	Mizusaki, Solid State Ionics 53-56, 791 (1992)	Extrapolated from 300 °C, assuming no association. Pure material shows -18 to -14 (anisotropy). Minimal change from NO ₃ or Ca doping. Li ₂ CO ₃ is only 1-2 orders lower than Na ₂ CO ₃ at 300–400 °C, but that extrapolates to 4–5 orders lower at 25 °C.
Li ₂ CO ₃ , PO ₄ -doped	-13 to -10	poly	Mizusaki, Solid State Ionics 53-56, 791 (1992)	Extrapolated from 300 °C, assuming no association. Need ~10 mol% PO ₄ doping to get 10 ⁻¹⁰ S cm ⁻¹ at 25 °C.

Table S2. Ionic conductivity at 25 °C of single-phase films as well as composite SEI layers. All values were measured by impedance spectroscopy. When necessary, extrapolations from measurements starting at 100–300 °C were used, as discussed in the notes.

Material	$\log_{10}(\sigma_{\text{ion}}(25\text{ °C}) / \text{S cm}^{-1})$	Reference	Notes
LiF	–13	Li, Adv. Funct. Mater., 21, 2901 (2011)	Refers to the conductivity far from the interface as given in Figure 6. Extrapolated from 270 °C.
Li ₂ O	–9	Guo, Chem. Mater., 32, 5525-5533 (2020)	Not clear if impedance analysis is entirely valid: low frequency arc was ignored, high frequency arc was fit by space charge capacitance and solid-state Warburg diffusion terms, etc. The associated error may be modest, e.g., including the low frequency resistance may only decrease the extracted conductivity by a factor of 2.
LiF	–9.3	Guo, Chem. Mater., 32, 5525-5533 (2020)	See above
Multiphase SEI	–9.3	Guo, Chem. Mater., 32, 5525-5533 (2020)	1 M LiPF ₆ EC/DEC electrolyte. SEI thickness of ~6 nm was not directly measured and may have substantial uncertainty.
Multiphase SEI (liquid electrolytes)	–9 to –7	Peled, J. Electrochem. Soc., 164, 7, A1703 (2017)	Page A1706 gives 10–1000 Ω cm ² for ~10 nm SEI, which corresponds to 10 ^{–7} to 10 ^{–9} S cm ^{–1} . Apparently agrees with Aurbach J Electroanal Chem, 348 (1994) estimate of 10 ^{–7} S cm ^{–1} .
Multiphase SEI (solid sulfide electrolytes)	–9.7 to –7	Wenzel, Solid State Ionics, 318, 102 (2018)	Based on 10-5000 Ω cm ² measured for ~10 nm SEI. Similar findings for LGPS and argyrodites given in Wenzel 2016 Chem Mater and Wenzel 2016 Solid State Ionics. Important that pressure was applied to improve solid–solid contact. SEI thickness not directly measured, may have ~10x uncertainty.