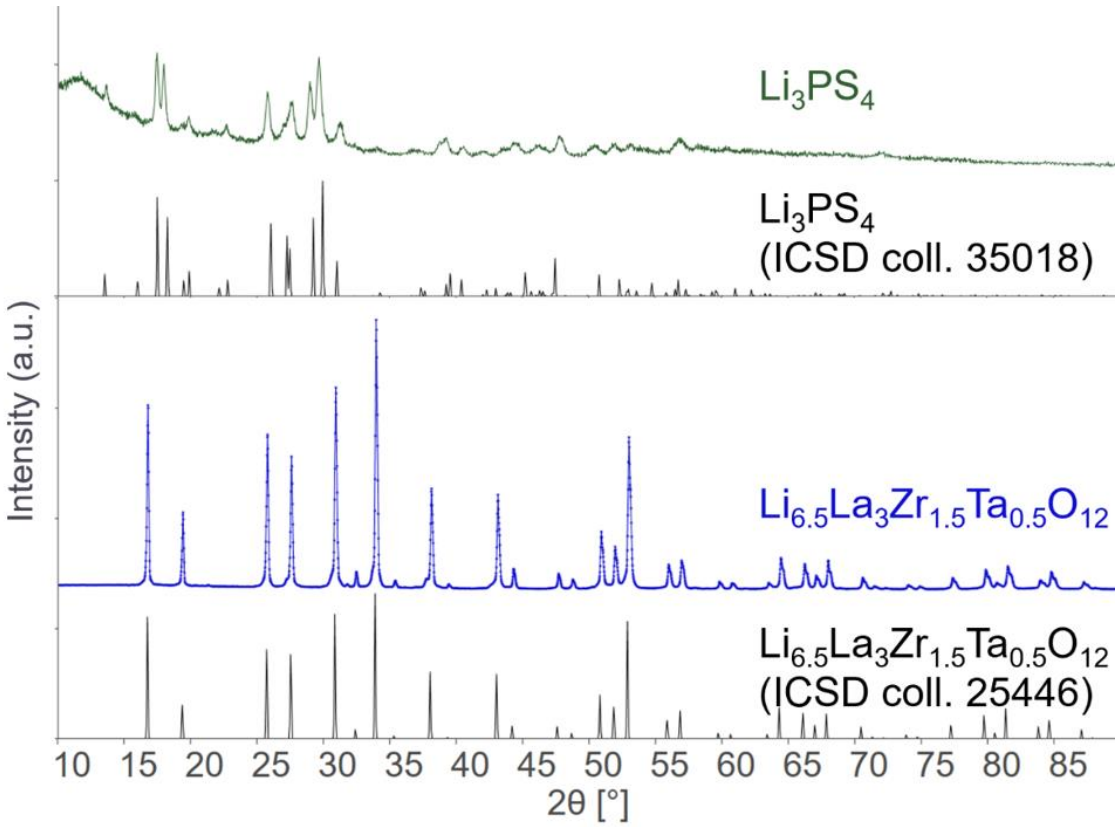

Figure S1. X-ray diffraction confirming the phase purity of Li_3Ps_4 (green) and $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (blue).

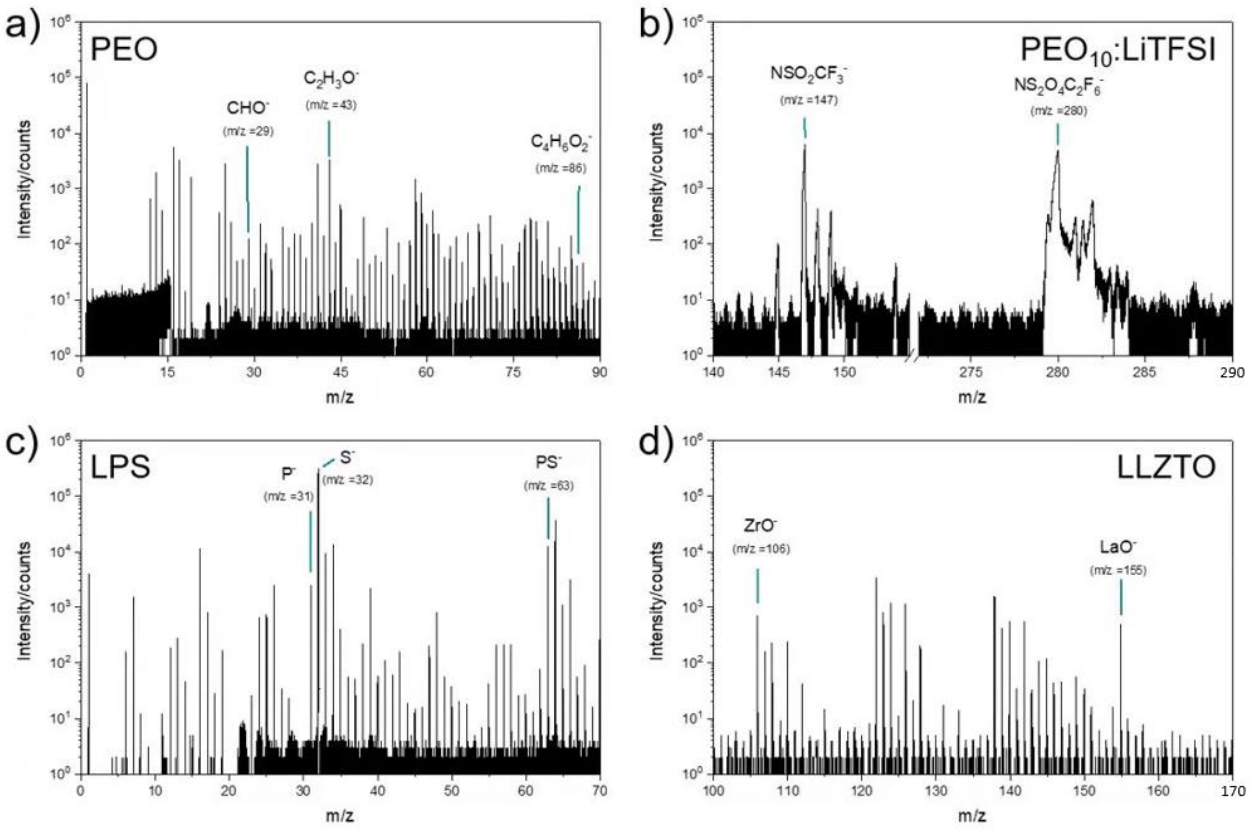

Figure S2. ToF-SIMS mass spectra of a) PEO; b) PEO_{10}LiTFSI; c) Li_3PS_4 (LPS); and d) $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO), with fragments of interest labelled.

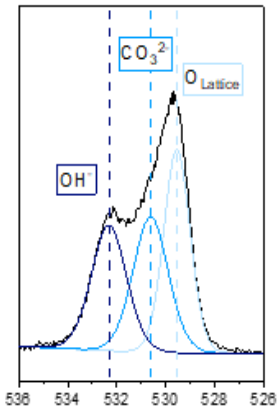

Figure S3. X-ray photoelectron spectroscopy showing the O 1s region of the spectrum of a pristine $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ electrolyte disk, showing the presence of both the $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ phase and carbonate and hydroxide impurities.

Table S1. Table showing the XPS binding energies and assignments of species at the SPE/LPS and SPE/LLZTO interfaces, relating to Figure 3. It should be noted that in the case of doublets, only the binding energy of the peak lowest in binding energy is given.

Interface	Region	Binding Energy (eV)	Assignment
PEO_{10}:LiTFSI / LPS	C 1s	284.4	$-(CH_2)-$ / C-C
		286.1	(OCH_2-CH_2-)
	S 2p	161.0	P-S-Li
		162.6	$-S_0-$ / P-S-P
		167.8	S=O
	P 2p	132.8	PS_4^{3-}
		133.8	PS_xO_y
PEO_{10}:LiTFSI / LLZTO	C 1s	286.0	(OCH_2-CH_2-)
		290.6	C-F
	O 1s	529.4	$O_{Lattice}$
		530.6	OH^-
		532.0	CO_3^{2-}
	Zr 3d	182.5	$Zr_{Lattice}$