All-solid-state Li-metal cell using nanocomposite TiO_2 /polymer electrolyte and self-standing $LiFePO_4$ cathode

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Supporting Information

Table S1: *Electrolyte resistance (R_e), interphase resistance (R_i), and chi-square value indicating the accuracy (χ^2) of the non-linear least squares (NLLS) analysis using the equivalent circuit $R_e(R_1C_1)(R_2C_2)Q_w$ on the EIS data of the symmetrical Li/membrane/Li cells with different polymer-to-salt ratio (EO/Li), collected at OCV of the cells and after 25 hours. See Figure 1b,d in the manuscript for related Nyquist plots.*

	Cell Condition	**R_e (Ω)**	**$R_i = R_1 + R_2$ (Ω)**	**$R = R_e + R_i$ (Ω)**	**χ^2**
EO/Li 18:1	OCV	18.7 ± 0.2	190 ± 11	209 ± 11	2×10^{-5}
	After 25 hours	3.6 ± 0.6	448 ± 6	452 ± 6	1×10^{-5}
EO/Li 21:1	OCV	11.0 ± 0.4	125 ± 6	136 ± 6	4×10^{-5}
	After 25 hours	13.3 ± 0.3	178 ± 11	191 ± 11	3×10^{-5}
EO/Li 25:1	OCV	10 ± 2	776 ± 13	786 ± 13	2×10^{-5}
	After 25 hours	24.3 ± 0.3	929 ± 8	953 ± 8	1×10^{-5}

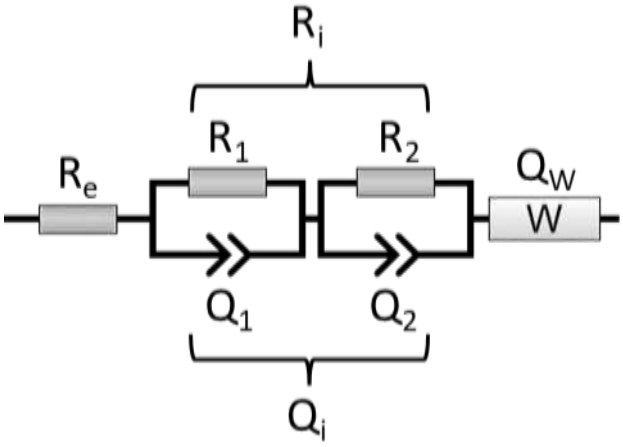

***Figure S1**: Representation of the equivalent circuit used in Figure 1b,d.*

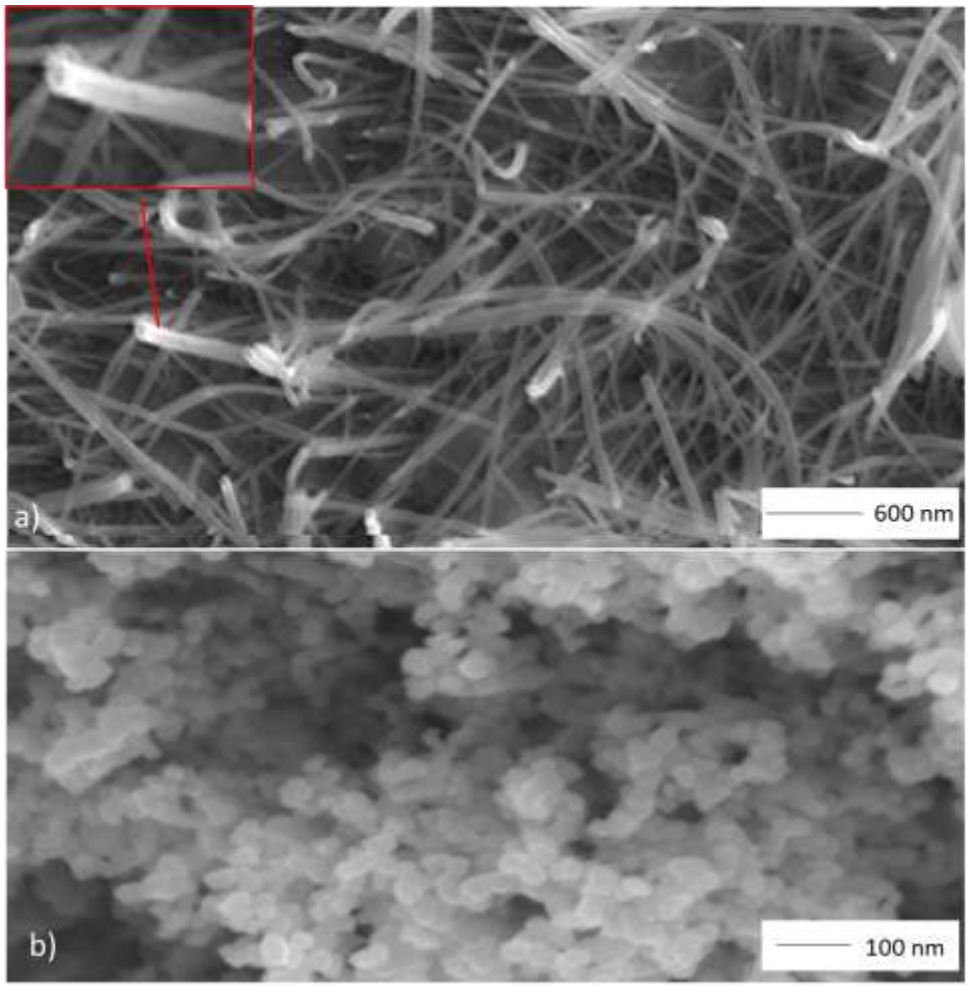

***Figure S2**: SEM images of **(a)** synthesized titanium dioxide nanotubes and **(b)** commercial P25 nanoparticles.*

Table S2: *Electrolyte resistance (R_e), interphase resistance (R_i), and chi-square value indicating the accuracy (χ^2) of the non-linear least squares (NLLS) analysis using the equivalent circuit $R_e(R_1C_1)(R_2C_2)Q_w$ on the EIS data of the symmetrical Li/membrane/Li cells with TiO_2 filler with different morphologies (nanotubes or nanoparticles) and concentration, collected at OCV of the cells and after 25 hours. See Figure 3 in the manuscript for related Nyquist plots.*

	Filler Concentration	**Cell Condition**	**R_e (Ω)**	**$R_i = R_1 + R_2$ (Ω)**	**χ^2**
Nanoparticles	NP15	OCV	17.0 ± 0.3	193 ± 14	2×10^{-5}
		After 25 hours	13.2 ± 0.2	445 ± 34	1×10^{-5}
	NP10	OCV	22.8 ± 0.9	78 ± 8	2×10^{-5}
		After 25 hours	18.3 ± 0.3	209 ± 18	2×10^{-5}
	NP3	OCV	22.8 ± 0.2	380 ± 10	7×10^{-6}
		After 25 hours	16.6 ± 0.2	437 ± 9	8×10^{-6}
Nanotubes	NT15	OCV	41.8 ± 0.2	103 ± 4	1×10^{-5}
		After 25 hours	25.9 ± 0.9	155 ± 11	5×10^{-5}
	NT10	OCV	21.1 ± 0.3	73 ± 4	1×10^{-5}
		After 25 hours	16.4 ± 0.3	91 ± 5	2×10^{-5}
	NT3	OCV	34.5 ± 0.6	254 ± 8	7×10^{-6}
		After 25 hours	21.6 ± 0.5	400 ± 10	1×10^{-5}

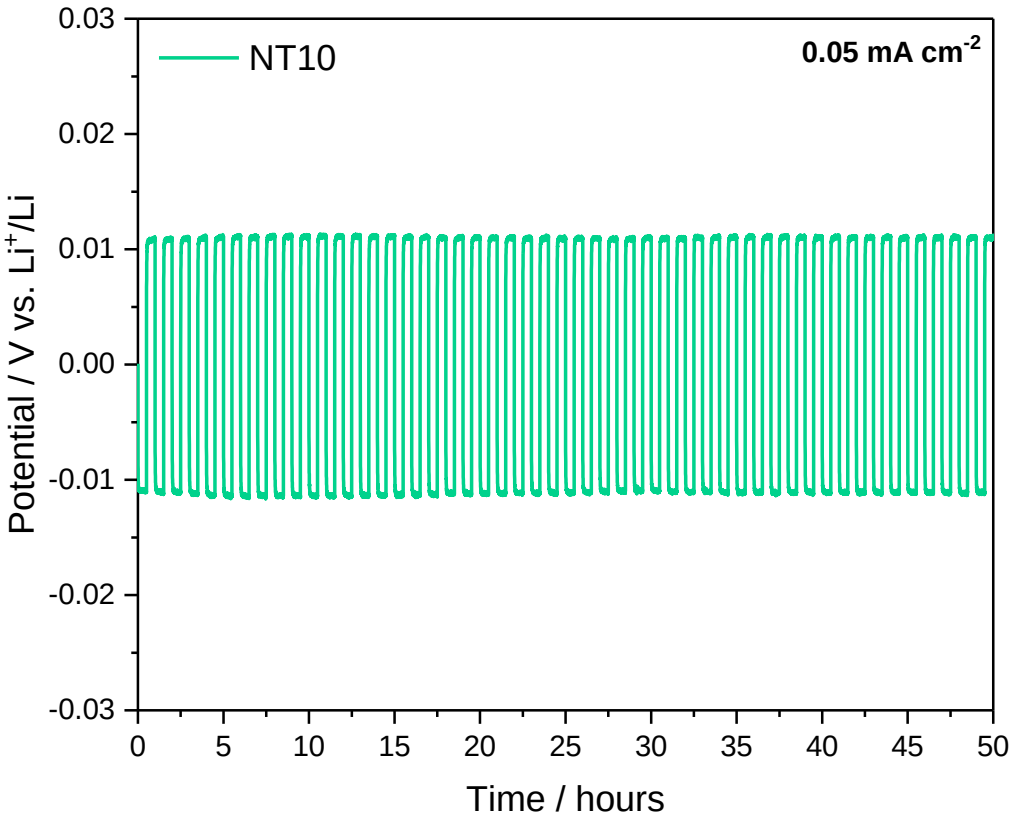

***Figure S3**: 50 hours of galvanostatic plating/stripping test performed on symmetrical Li/NT10/Li cells. I = 0.05 mA cm^{-2}; T = 65 °C.*

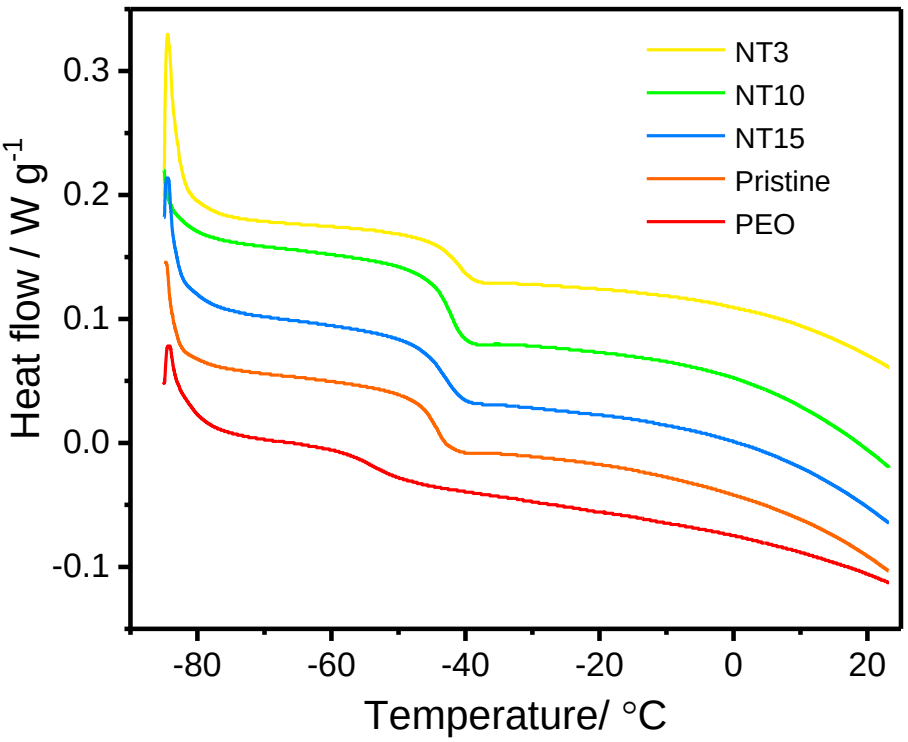

Figure S4: *Differential Scanning Calorimetry curves of PEO polymer (red), pristine membrane (orange), NT15 (blue), NT10 (green), and NT3 (yellow) recorded under nitrogen flow in the -80 – 25 °C temperature range.*

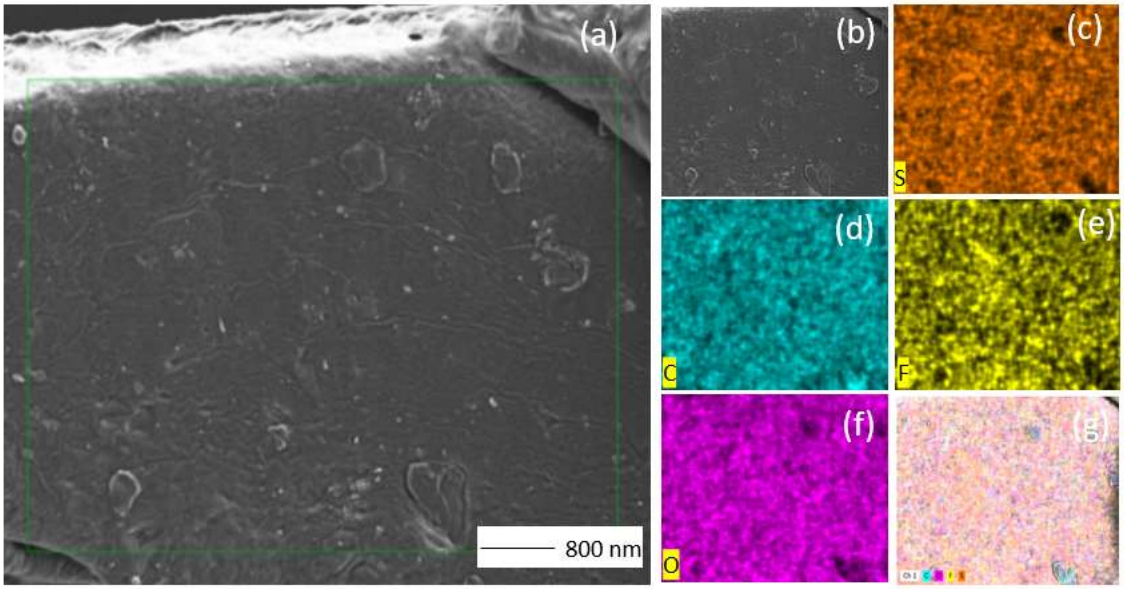

Figure S5: *(**a**) SEM image of the pristine membrane, (**b**) EDS mapping of (**c**) sulfur (**d**) carbon (**e**) fluorine and (**f**) oxygen. (**g**) Overlapping of all the elements detetected by EDS.*

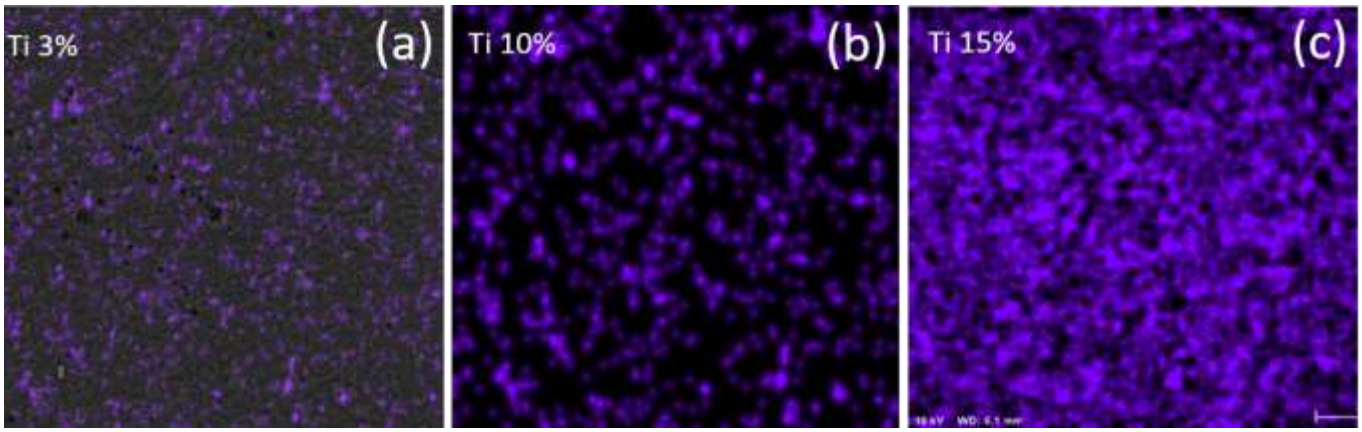

Figure S6: *EDS elemental maps of different concentrations of TiO_2 in* ***(a)*** *NT3,* ***(b)*** *NT10, and* ***(c)*** *NT15.*

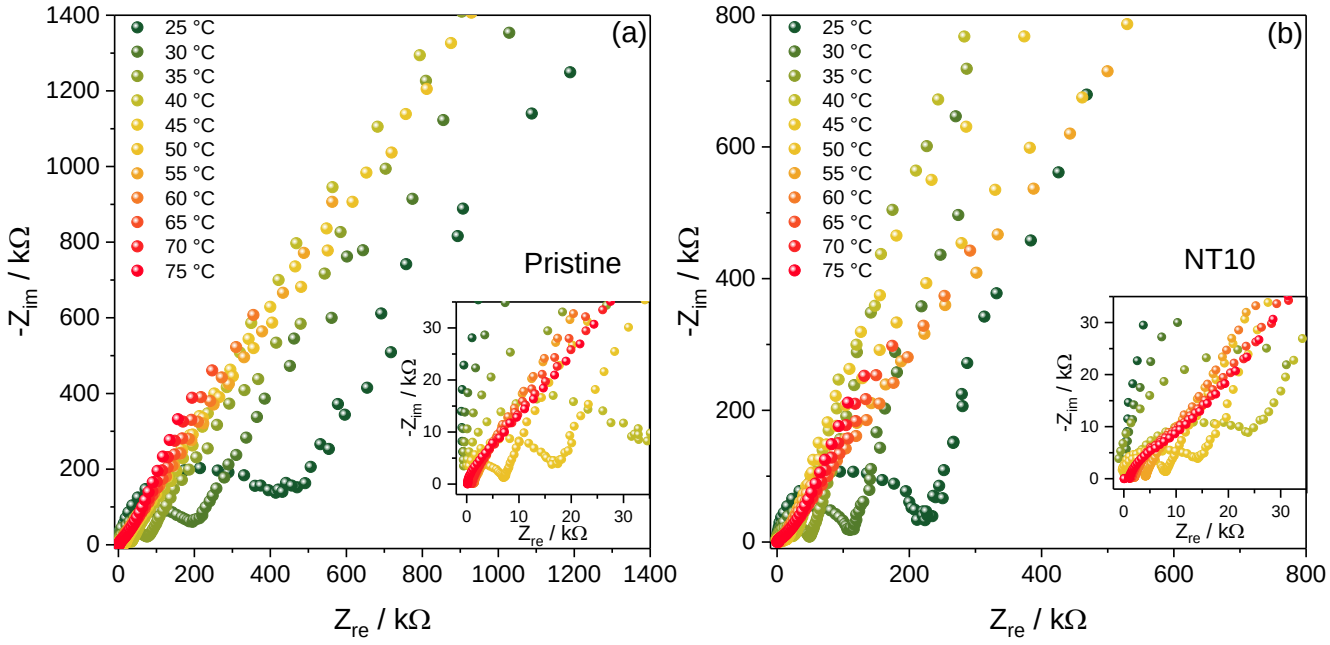

Figure S7: *Nyquist plots related to EIS measurements performed at various temperatures on a stainless-steel/membrane/stainless-steel symmetrical cell with* ***(a)*** *pristine membrane and* ***(b)*** *NT10 to evaluate the electrolyte ionic conductivity, with magnification of the high-frequency region in the insets.*

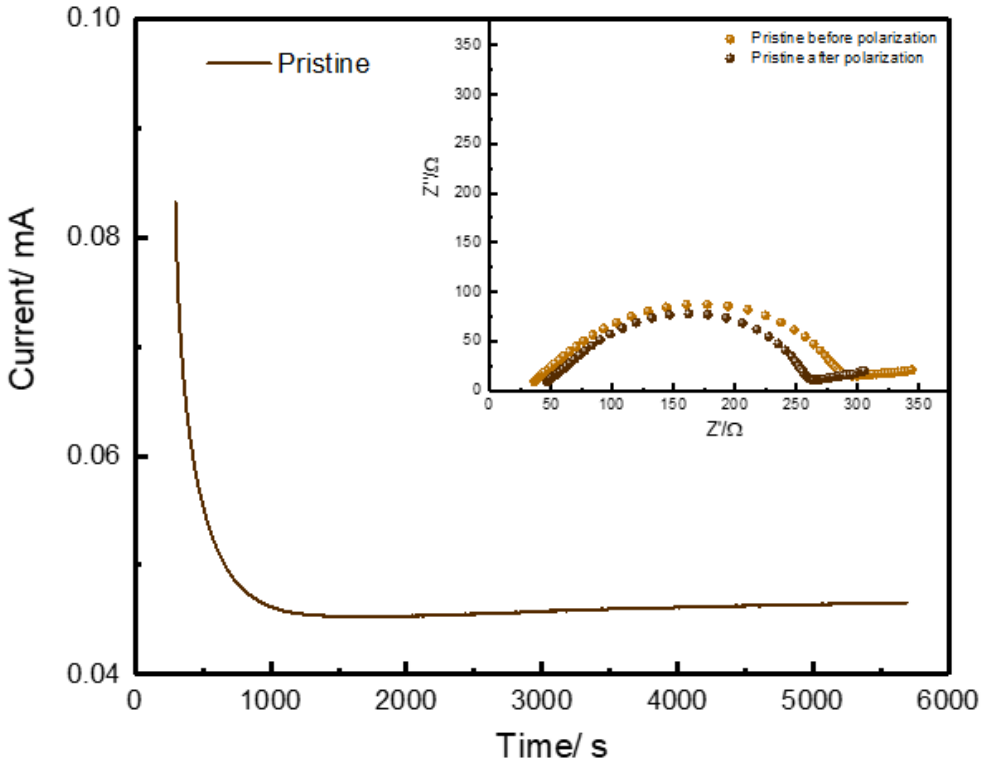

***Figure S8**: Chronoamperometry curve recorded on a Li/Li symmetrical cell using pristine membrane as electrolyte for determination of Li^+ transference number at 65 °C. The inset displays the corresponding Nyquist plots obtained by EIS at the initial and steady state.*

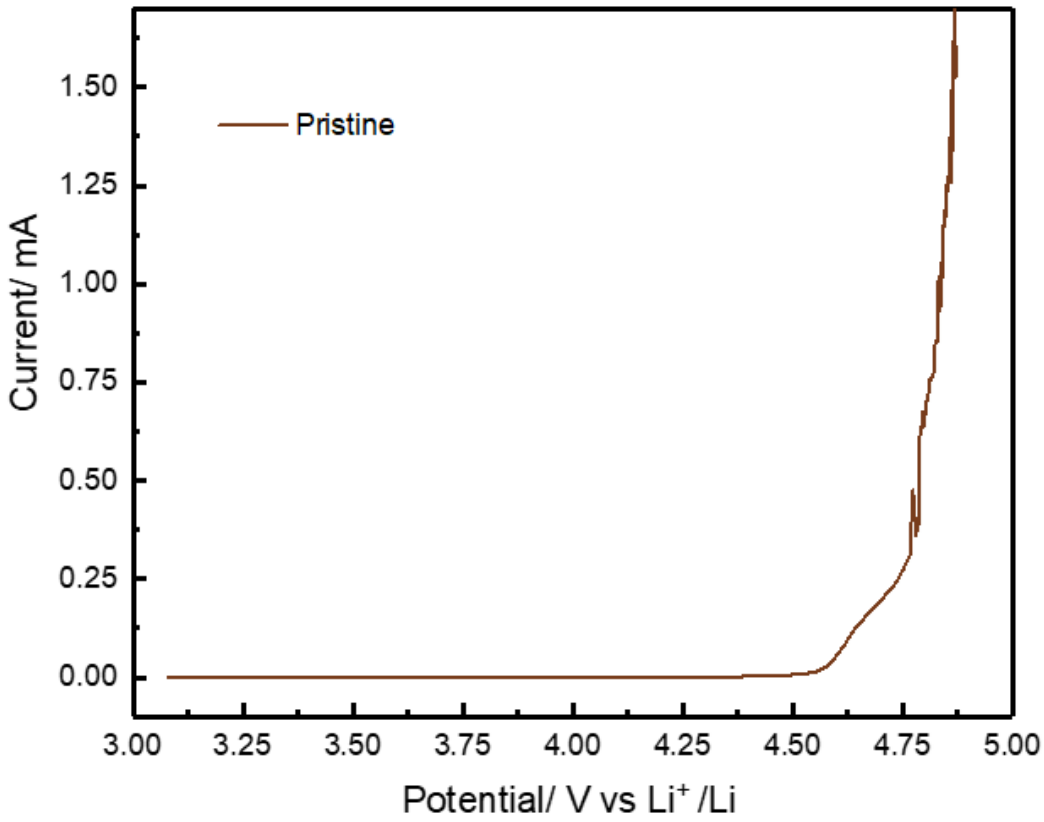

***Figure S9**: Linear sweep voltammetry in anodic region (OCV – 5 V vs. Li^+/Li potential range) performed at 65 °C in lithium cell using the pristine membrane as the electrolyte and Super P carbon coated on aluminium as the working electrode.*

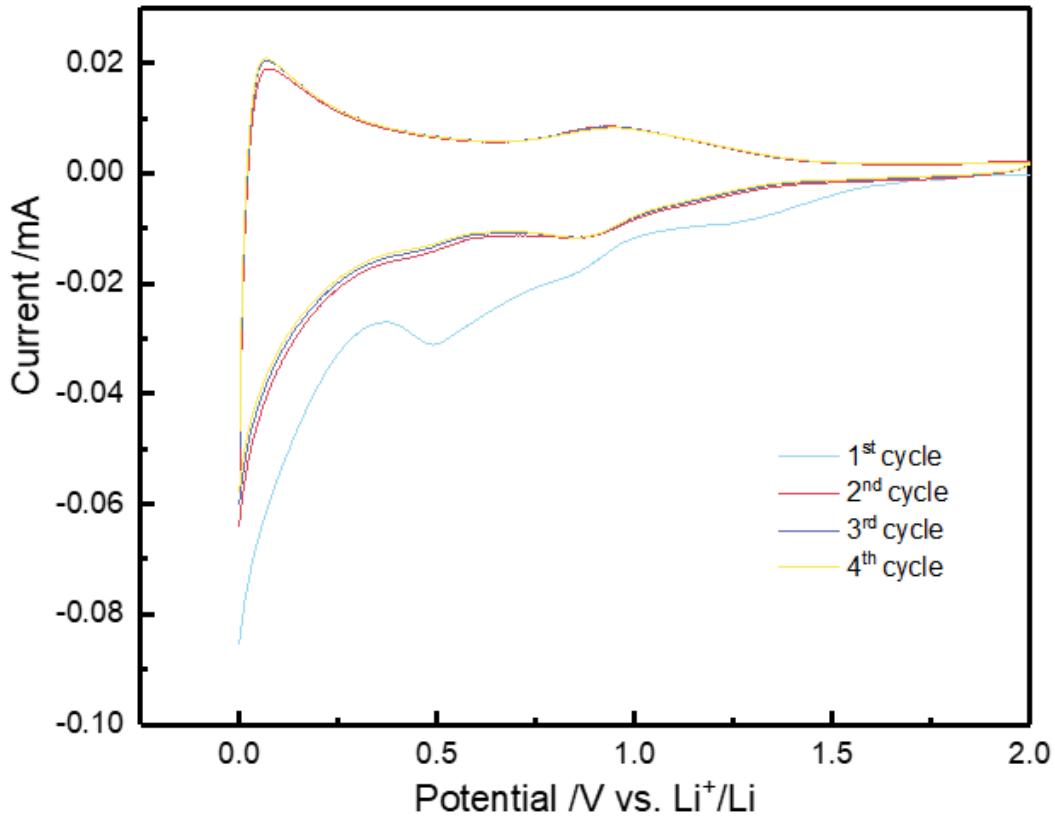

***Figure S10**: CV curve of the cathodic region (0.01 – 2 V vs. Li^+/Li potential range) performed at 65 ° using the NT10 membrane as the electrolyte and Super P carbon coated on copper as the working electrode.*

Table S3: *NLLS analysis on the Nyquist plots reported in Figure 7d in the manuscript collected by EIS on a Li/NT10/Li symmetrical cell upon aging. The NLLS fitting was performed through the RelaxIS3 software, and the corresponding resistance trend is shown in Figure 7e in the manuscript.*

Cell Condition	Equivalent Circuit	$R_i = R_1 + R_2$ (Ω)	χ^2
After 1 hour	$R_e(R_1C_1)(R_2C_2)Q_w$	90	3×10^{-5}
After 3 hours	$R_e(R_1C_1)(R_2C_2)Q_w$	95	6×10^{-6}
After 8 hours	$R_e(R_1C_1)(R_2C_2)Q_w$	102	5×10^{-6}
After 20 hours	$R_e(R_1C_1)(R_2C_2)Q_w$	108	7×10^{-6}
After 32 hours	$R_e(R_1C_1)(R_2C_2)Q_w$	104	7×10^{-6}
After 2 days	$R_e(R_1C_1)(R_2C_2)Q_w$	103	7×10^{-6}
After 2.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	104	7×10^{-6}
After 3 days	$R_e(R_1C_1)(R_2C_2)Q_w$	103	2×10^{-5}
After 3.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	100	2×10^{-5}
After 4 days	$R_e(R_1C_1)(R_2C_2)Q_w$	99	8×10^{-6}
After 4.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	98	6×10^{-6}
After 5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	99	9×10^{-6}
After 5.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	98	1×10^{-5}
After 6 days	$R_e(R_1C_1)(R_2C_2)Q_w$	98	1×10^{-5}
After 6.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	97	1×10^{-5}
After 7 days	$R_e(R_1C_1)(R_2C_2)Q_w$	96	1×10^{-5}
After 7.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	96	1×10^{-5}
After 8 days	$R_e(R_1C_1)(R_2C_2)Q_w$	95	9×10^{-6}
After 8.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	94	1×10^{-5}
After 9 days	$R_e(R_1C_1)(R_2C_2)Q_w$	95	1×10^{-5}
After 9.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	95	9×10^{-6}
After 10 days	$R_e(R_1C_1)(R_2C_2)Q_w$	96	9×10^{-6}
After 10.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	97	9×10^{-6}
After 11 days	$R_e(R_1C_1)(R_2C_2)Q_w$	98	9×10^{-6}
After 11.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	99	8×10^{-6}
After 12 days	$R_e(R_1C_1)(R_2C_2)Q_w$	100	9×10^{-6}
After 12.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	101	8×10^{-6}
After 13 days	$R_e(R_1C_1)(R_2C_2)Q_w$	103	8×10^{-6}
After 13.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	104	8×10^{-6}
After 14 days	$R_e(R_1C_1)(R_2C_2)Q_w$	105	8×10^{-6}
After 14.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	107	8×10^{-6}
After 15 days	$R_e(R_1C_1)(R_2C_2)Q_w$	110	1×10^{-5}
After 15.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	110	7×10^{-6}
After 16 days	$R_e(R_1C_1)(R_2C_2)Q_w$	112	7×10^{-6}
After 16.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	114	7×10^{-6}
After 17 days	$R_e(R_1C_1)(R_2C_2)Q_w$	115	7×10^{-6}
After 17.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	117	7×10^{-6}
After 18 days	$R_e(R_1C_1)(R_2C_2)Q_w$	118	7×10^{-6}
After 18.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	120	5×10^{-6}
After 19 days	$R_e(R_1C_1)(R_2C_2)Q_w$	122	5×10^{-6}
After 19.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	123	5×10^{-6}

After 20 days	$R_e(R_1C_1)(R_2C_2)Q_w$	125	5×10^{-6}
After 20.5 days	$R_e(R_1C_1)(R_2C_2)Q_w$	128	4×10^{-6}

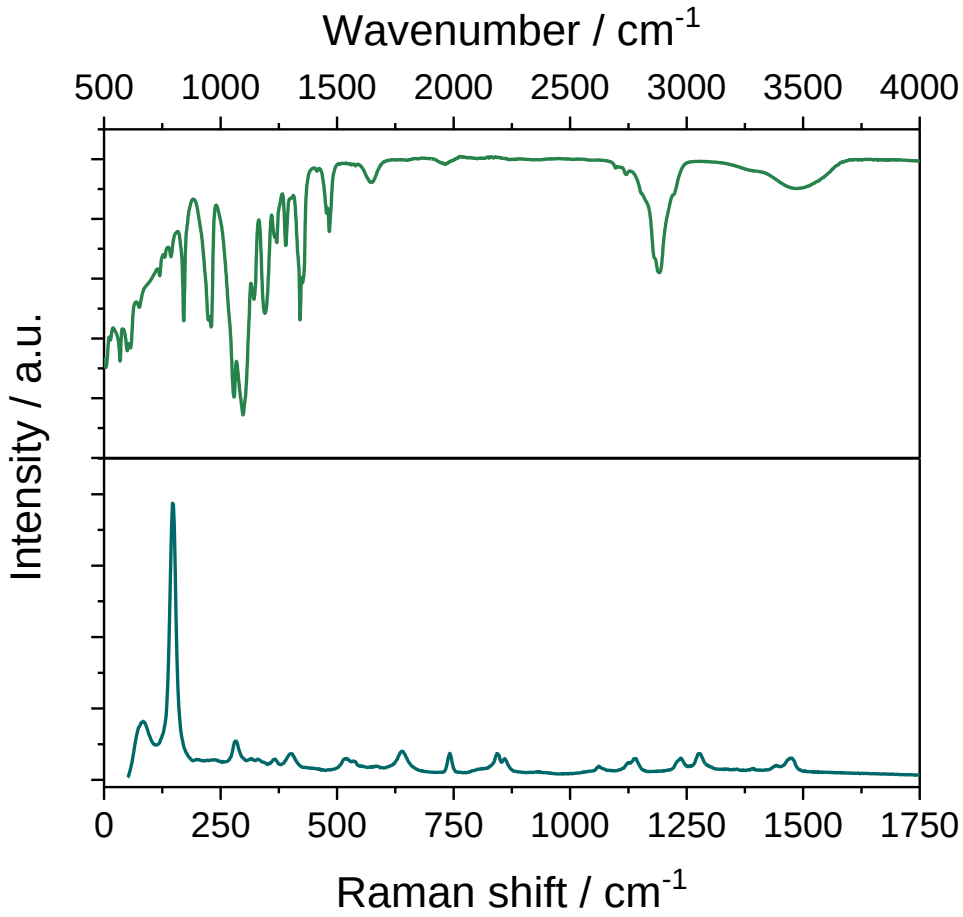

Figure S11: *IR spectrum (top panel), recorded in the 500 – 4000 cm^{-1} range, and Raman spectrum (bottom panel), recorded in the 0 – 1750 cm^{-1} range, of the NT10.*

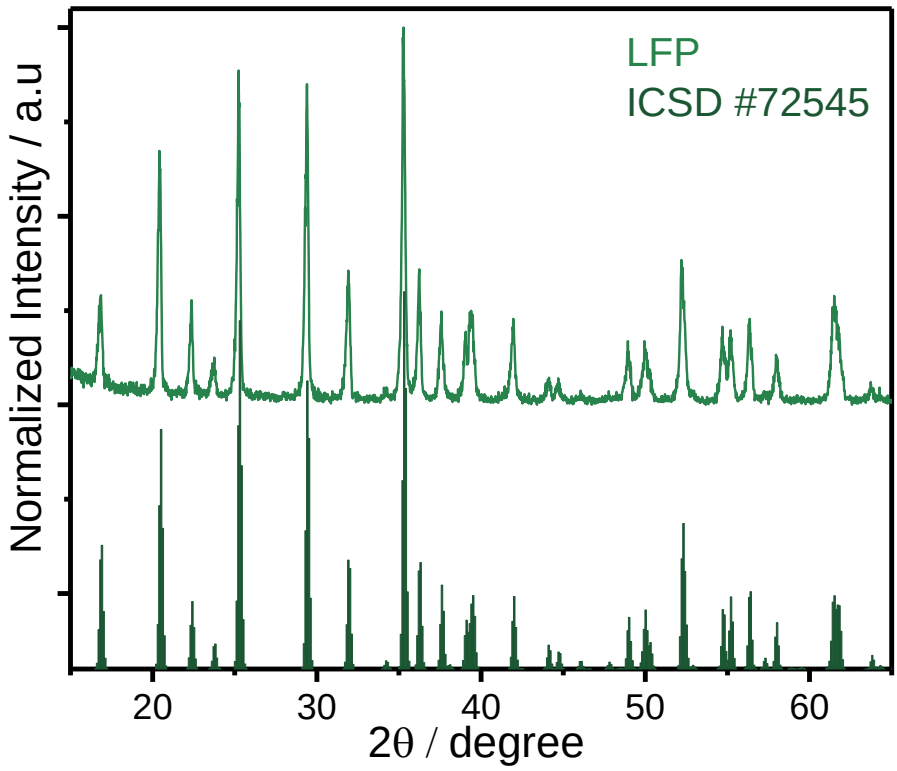

Figure S12: *XRD pattern of commercial LFP powder compared to corresponding reference diffractogram (ICSD #72545).*

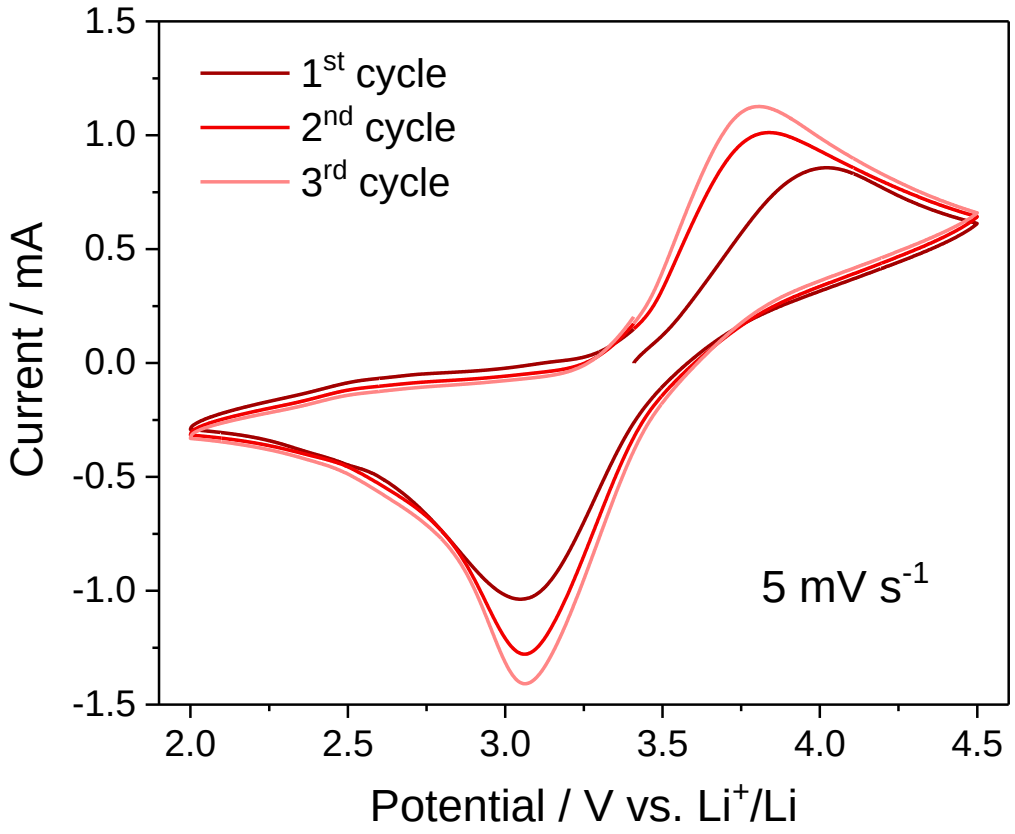

Figure S13: *CV measurement performed on the Li/NT10/SS_LFP cell in the potential range 2.5 – 4.5 V vs. Li^+/Li at the scan rate of 5 mV s^{-1}.*