### **Electronic Supplementary Information**

#### SI 1. Syntheses

#### SI 1.1. Materials

All commercially purchased chemicals were used as received unless otherwise stated. 1,4-Butanediol (>99%) and 1,6-Hexanediol (97%) were purchased from Acros Organics. Triethylamine (>99.5%), Pyridine (>99%), 2-Hydroxyethylmethacrylate (HEMA, >99%), Methyl-2-chloro-2-oxoacetate (96%), Methyl-3-chloro-3-oxopropionate (97%), Methyl-4-chloro-4-oxobutyrate (97%), 4-Hydroxybutylacrylate (>97%), Butylacrylate (BA, >99%), Polycaprolactone (PCI), Methyladipoylchloride (97%), Bis(trifluoromethylsulfonyl)amine lithium salt (LiTFSI, 99.95%, trace metal basis) and lithium ribbon (99.9%, trace metal basis, 380 μm) were purchased from Sigma Aldrich. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma Aldrich and purified by recrystallization in methanol before use. Methacryloylchloride (97%) was purchased from Sigma Aldrich and purified by vacuum distillation. Bis(fluorosulfonyl)imide lithium salt (LiFSI, 98%) was purchased from TCI. Diethyl ether (>=99.5%, analytical reagent grade), Methanol (>=99.9%, analytical reagent grade), 1,4-Dioxane (>=99.8%, analytical reagent grade) and Acetonitrile (>=99.9%, HPLC gradient grade) were purchased from Fisher Scientific. Dichloromethane (>=99.5%, stabilized with 0.2% Ethanol) and n-Hexane (>=98%) were purchased from VWR Chemicals. P25 (TiO<sub>2</sub> nanoparticles, 21 nm primary particle size) was procured from Degussa. CR2032 coin cell cases (20d x 3.2t mm) with gaskets, wave springs and stainless-steel spacers were purchased from MTI corporation/PI KEM. LiFePO<sub>4</sub>, Super P carbon, conductive graphite and C-coated AI current collector were procured from MTI. ipPORE<sup>™</sup> track-etched hydrophilic Polyimide (PI) membranes (pore size: 0.20 μm, pore density: 6.00.10<sup>8</sup> cm<sup>-2</sup>, thickness: 8 μm) were purchased from it4ip (Belgium).

#### SI 1.2. Characterization

<sup>1</sup>**H-NMR spectroscopy.** <sup>1</sup>**H-NMR** spectra were recorded on a Bruker Avance AC250 Spectrometer at a working frequency of 300 MHz. The obtained spectra (64 scans) were calibrated to the corresponding residual solvent peak with CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm) or DMSO-*d*6 ( $\delta$  = 2.50 ppm), respectively. Chemical shifts are given in ppm, coupling constants (J) are reported in hertz (Hz, and multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (quintuplet), hept (septuplet) or m (multiplet).

**Size Exclusion Chromatography (SEC).** SEC was measured utilizing a Waters 515 HPLC pump and THF with 0.25 wt % tetrabutylammonium bromide (TBAB) as eluent at a flow rate of 0.5 mL min<sup>-1</sup>. 100  $\mu$ L of polymer solution (1–2 mg mL<sup>-1</sup>) are injected by a 707 Waters autosampler into a column setup comprising a guard column (Agilent PLgel Guard MIXED-C, 5cm × 0.75 cm, particle size 5  $\mu$ m) and two separation columns (Agilent PLgel MIXED-C, 30 cm × 0.75 cm, particle size 5  $\mu$ m). Polymer size distributions were monitored by a Waters 414 refractive index detector. Polystyrene (PS) standard was used for calibration and 1,2-dichlorobenzene was used as an internal reference.

**Differential Scanning Calorimetry (DSC).** DSC thermograms were obtained using a Mettler Toledo DSC 3. The samples were sealed witin aluminum crucibles. The temperature program comprised two cycles of cooling down to -80 °C and subsequent heating up to 150 °C or 200 °C at a cooling/heating rate of 10 K min<sup>-1</sup>. For the third cycle, a cooling/heating rate of 40 K min<sup>-1</sup> was chosen. Glass transition temperatures ( $T_g$ ) are derived as inflection points of the transition temperature and melting points ( $T_m$ ) are obtained as the peak maximum of the melting peak in the second heating curve.

**Thermogravimetric Analysis (TGA).** TGA thermograms were recorded on a Mettler Toledo TGA/DSC 3. Samples (ca. 10 -20 mg) were placed in aluminum oxide ceramic crucibles (70  $\mu$ L) and heated from 30 to 700 °C at a heating rate of 10 K min<sup>-1</sup> under nitrogen atmosphere.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). Infrared (IR) absorption experiments were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer. The spectra were recorded from solids in attenuated total reflectance mode in the form of transmission data normalized between 0 and 100. The data were initially transformed to absorbance data between 0 and 1.

The deconvolution process using a (double-peak) Gaussian nonlinear fitting was performed by a Levenberg Marquardt Iteration Algorithm (4 parameters for each of both peaks). In the case of pristine polymers without salt-addition, a single-peak fit was performed. The following equation was fitted to the normalized absorbance data:

$$y = y_0 + \frac{A}{w \cdot \sqrt{\frac{\pi}{4 \cdot \ln 2}}} \cdot exp^{\left(-4 \cdot \ln 2 \cdot \frac{\left(x - x_c\right)^2}{w^2}\right)}$$

with  $x_c$  as the expected value (center),  $w^2$  as the variance,  $y_0$  as y-axis offset and A as the area of the distribution function. Within each fitted curve, the  $y_0$  y-axis offset was set constant for both peaks. Furthermore, within each fitted curve the  $x_c$  expected value of the peak (distribution) was manually picked to the visible peak center and set fixed for the fitting. Towards higher salt contents, the peak wavenumbers shift towards higher values. The molar fraction of carbonyl units registering the influence (proximity) of Li<sup>+</sup> cations (Li<sup>+</sup>-"coordinated" carbonyls)  $f_{Li^+}$  was calculated as ratio of the peak area  $A_{C=O-Li^+}$  of the shifted peak vs. peak area of both peaks  $A_{C=O-Li^+} + A_{C=O}$ 

(formula S1)

$$f_{Li^{+}} = \frac{A_{C=0-Li^{+}}}{A_{C=0-Li^{+}} + A_{C=0}}$$
 (formula S2)

Table S1. Fitting parameters and calculated  $f_{Li+}$  value for the double-/single-peak Gaussian nonlinear fitting of the FTIR curves for the PMA4.2 salt screening as well as the comparison of PBA1-25T and PA4.4-25T.

		1 <sup>st</sup> peak (C=	:O)	2 <sup>nd</sup> peak (C=O-Li <sup>+</sup> )					
Sample	y <sub>0</sub>	x <sub>c</sub> (fixed)	А	w	¥٥	x <sub>c</sub> (fixed)	Α	w	f <sub>Li+</sub>
PMA4.2	0.00090	1725	0.801	38.7		-		-	
	±0.00004	1725	±0.006	±0.3	-		-		
DNAA 2 10T	0.00084	1720	0.559	34.7	0.00084	1702	0.255	34.2	0.31
PIVIA4.2-101	±0.00003	1/50	±0.004	±0.3	±0.00003	1705	±0.004	±0.7	
PMA4.2-25T	0.00124	1720	0.401	32.8	0.00124	1702	0.325	30.9	0.45
	±0.00005	1/50	±0.006	±0.6	±0.00005	1705	±0.006	±0.6	
PMA4.2-50T	0.00133	1720	0.245	30.0	0.00133	1702	0.460	30.3	0.65
	±0.00005	1750	±0.007	±0.9	±0.00005	1705	±0.007	±0.5	
PMA4.2-70T	0.00176	1727	0.196	25.7	0.00176	1706	0.416	28.0	0.68
	±0.00006	1/2/	±0.008	±1.2	±0.00006	1700	±0.009	±0.7	
PMA4.2-80T	0.00221	1725	0.061	30.3	0.00221	1715	0.451	33.7	0.88
	±0.00009	1/35	±0.014	±6.4	±0.00009	1/15	±0.015	±1.0	
PA4.4-25T	0.001	1722	0.382	28.7	0.001	1702	0.396	30.1	0.51
	±0.00003	1/32	±0.014	±0.7	±0.00003	1703	±0.014	±0.7	0.51
PBA1-25T	0.00096	1721	0.419	26.2	0.00096	1702	0.369	28.9	0.47
	±0.00003	1/31	±0.008	±0.4	±0.00003	1/02	±0.008	±0.5	

Scanning Electron Microscopy (SEM). The surface morphology was analyzed using a Zeiss LEO 1530 scanning electron microscope.

#### SI 1.3. General procedures

The esterification of an alcohol and an acyl chloride.<sup>[1,2]</sup> The alcohol and a sterically hindered organic nitrogen-base (e.g. triethylamine, pyridine) are dissolved in dichloromethane (DCM, ca. 2x weight of alcohol). The mixture is dried for ca. 30 min by addition of a small amount of  $CaH_2$  under stirring and consequently filtered over a short neutral  $Al_2O_3$ -column into a flame-dried, argon-filled Schlenk round-bottom flask. The mixture is heavily stirred and cooled to 0 °C by an ice bath. Meanwhile, the acyl chloride is weighed out quickly (moisture sensitive), dissolved in ca. 4-fold excess of DCM and put into a dropping funnel. From there, it is dropwise added to the cooled alcohol/base mixture under heavy stirring. After a few minutes, a white solid precipitate becomes visible due to the formation of the insoluble nitrogen-base hydrochloride salt. After all acyl chloride is added, the ice bath is removed, and the solution is stirred overnight. Complete conversion is confirmed by <sup>1</sup>H NMR.

In the synthesis of 4HBMS and 6HHM, a diol (double-functionalized alcohol) is to be mono-esterified at only one side. Therefore, a 10-fold excess of diol and a twofold excess of base with respect to the acyl chloride is applied to minimize double-functionalization. The excess diols as well as the nitrogen-base/corresponding hydrochloride salt are highly water-soluble and can therefore easily be removed during the washing procedure. In the case of all other esterifications with only one hydroxy-group, excess chloride and nitrogen-base is utilized to ensure complete alcohol conversion. Non-reacted acyl chloride hydrolyzes immediately upon contact with water to form the corresponding carboxylic acid, which is also highly water-soluble and can easily be removed by washing with water.

For the purification, the DCM volume is roughly doubled by the addition of *n*-Hexane to precipitate most of the nitrogen-base hydrochloride salt. The mixture is filtered through a paper filter which is then rinsed with n-Hexane. After removal of the solvent at the rotary evaporator, the crude product is re-dissolved in ca. 10-fold excess of DCM and then washed three times, each time in a way that organic and aqueous phase have roughly the same volume: first with a saturated aqueous solution of  $NH_4CI$  (weakly acidic to protonate excess organic base) and then twice with DI water. After each washing step, the aqueous phase is additionally extracted three times with a small amount of DCM. Thereafter, the combined organic phases are dried with MgSO<sub>4</sub>, filtered through a paper filter, and dried at the rotary evaporator to yield the product ester in high purity.

The free radical polymerization of acrylate and methacrylate monomers. The purified monomers and recrystallized 2,2'-Azobis(2-methylpropionitrile) (AIBN) are weighed out, combined, and dissolved in 1,4-Dioxane. The mixture is filtered through a short column filled with neutral  $Al_2O_3$  to remove all traces of stabilizer (originating from the acrylate/methacrylate compounds) directly into a flame-dried Schlenk round-bottom flask equipped with a magnetic stir bar. The flask is sealed by a ribbon stopper und degassed by bubbling argon gas via a syringe through the solution for ca. 30 min under stirring. The polymerization is started by rapid heating to 75 °C (pre-warmed heater) under heavy stirring. The polymerizations are always run overnight and terminated after at least 20 h by cooling down to room temperature. Conversion is determined by <sup>1</sup>H NMR spectroscopy.

For all polymers, 1 mol-% of AIBN with respect to the monomer is applied. The monomer concentration is varied and optimized individually for the various monomers.

For the purification, most of the solvent is removed to obtain a highly viscous polymer solution, which is dropwise precipitated in stirred *n*-Hexane and/or  $Et_2O$  and/or MeOH (sequentially). The solvent is then decanted (in the case of very fine precipitation, centrifugation is applied to enhance the solid/liquid separation). Thereafter, the polymer is re-dissolved in DCM, filtered through a paper filter and dried first at the rotary evaporator and then in the drying furnace at 90 °C in high vacuum overnight.

#### SI 1.4. 4-hydroxybutyl methyl succinate (4HBMS), 4-(methacryloyloxy)butyl methyl succinate MA4.2 & Poly[4-(methacryloyloxy)butyl methyl succinate] PMA4.2

**Synthesis of 4-hydroxybutyl methyl succinate (4HBMS).** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 1,4-Butanediol (100 g, 1.110 mol, 10.0 eq.), Triethylamine (30.62 g, 0.303 mol, 2.73 eq.) and Methyl-4-chloro-4-oxobutyrate (21.34 g, 0.142 mol, 1.23 eq.) were deployed.

Yield: 23.64 g (81%), yellow oil.

After the general workup procedure, rests of di-substituted ester could be observed in <sup>1</sup>H NMR. Therefore, the product was further purified by distillation ( $T_{\text{bath}}$ : 150 °C,  $T_{\text{bridge}}$ : 120 °C, p: 4.8-10<sup>-6</sup> bar).

Yield<sub>distilled</sub>: 20.09 g (69%), colorless liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.43 (t, J = 5.1 Hz, 1H<sub>a</sub>), 4.02 (t, J = 6.6 Hz, 2H<sub>b</sub>), 3.59 (s, 3H<sub>c</sub>), 3.40 (td, J = 6.3, 5.1 Hz, 2H<sub>d</sub>), 2.55 (d, J = 1.7 Hz, 4H<sub>e</sub>), 1.66 - 1.51 (m, 2H<sub>f</sub>), 1.45 (dd, J = 8.0, 1.0 Hz, 2H<sub>g</sub>).

**Synthesis of 4-(methacryloyloxy)butyl methyl succinate MA4.2.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 4-hydroxybutyl methyl succinate (4HBMS; 7.620 g, 0.037 mol, 1.00 eq.), Triethylamine (7.55 g, 0.075 mol, 2.00 eq.) and distilled Methacryloylchloride (5.851 g, 0.056 mol, 1.5 eq.) were deployed. The workup procedure was extended by three additional washing cycles in *n*-Hexane against DI-water.

Yield: 9.25 g (91%), pale-yellow clear liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.02 (dq, J = 2.0, 1.0 Hz, 1H<sub>a</sub>), 5.68 (p, J = 1.6 Hz, 1H<sub>b</sub>), 4.16 – 4.08 (m, 2H<sub>c</sub>), 4.08 – 4.00 (m, 2H<sub>d</sub>), 3.59 (s, 3H<sub>e</sub>), 2.55 (s, 4H<sub>f</sub>), 1.88 (dd, J = 1.6, 1.0 Hz, 3H<sub>g</sub>), 1.74 – 1.57 (m, 4H<sub>h</sub>).

**Synthesis of Poly[4-(methacryloyloxy)butyl methyl succinate] PMA4.2.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 4-(methacryloyloxy)butyl methyl succinate MA4.2 (9.270 g, 34.0 mmol, 1.00 eq.) and AIBN (0.056 g, 0.34 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (85 g) to adjust a monomer-concentration of ca. 10 wt%. After 24 h, ca. 88% conversion was obtained. The polymer was purified by precipitation in  $Et_2O$  and *n*-Hexane.

Yield: 5.91 g (64 %); clear, amorphous yellow viscous polymer

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  3.98 (m, J = 39.5 Hz, 4H<sub>a</sub>), 3.59 (s, 3H<sub>b</sub>), 2.56 (s, 4H<sub>c</sub>), 1.63 (s, 4H<sub>d</sub>), 0.76 (m, 5H<sub>e</sub>). SEC:  $M_n$  = 13700 g mol<sup>-1</sup>,  $M_p$  = 25900 g mol<sup>-1</sup>, D = 2.43.

DSC:  $T_{g}$  = -37 °C, no  $T_{m}$ TGA:  $T_{5\%}$  = 280 °C



Figure S1a. <sup>1</sup>H NMR spectra of 4HBMS (top), MA4.2 (middle) and PMA4.2 (bottom) including integrals and peak assignments.

#### SI 1.5. 6-hydroxyhexyl methacrylate (6HHM), 6-(methacryloyloxy)hexyl methyl succinate MA6.2 & Poly[6-(methacryloyloxy)hexyl methyl succinate] PMA6.2

**Synthesis of 6-hydroxyhexyl methacrylate (6HHM).** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 1,6-Hexanediol (101.06 g, 0.855 mol, 10.00 eq.), Triethylamine (17.30 g, 0.171 mol, 2.00 eq.) and distilled Methacryloylchloride (9.04 g, 0.086 mol, 1.01 eq.) were deployed.

Yield: 13.87 g (86%), pale-yellow oil.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.01 (dq, J = 1.9, 1.0 Hz, 1H<sub>a</sub>), 5.67 (p, J = 1.6 Hz, 1H<sub>b</sub>), 4.36 (t, J = 5.1 Hz, 1H<sub>c</sub>), 4.08 (t, J = 6.6 Hz, 2H<sub>d</sub>), 3.40 - 3.29 (m, 2H<sub>e</sub>), 1.87 (dd, J = 1.6, 1.0 Hz, 3H<sub>f</sub>), 1.68 - 1.53 (m, 2H<sub>g</sub>), 1.48 - 1.23 (m, 6H<sub>h</sub>).

**Synthesis of 6-(methacryloyloxy)hexyl methyl succinate MA6.2.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 4-hydroxyhexyl methacrylate (6HHM; 4.675 g, 0.025 mol, 1.00 eq.), Triethylamine (5.08 g, 0.050 mol, 2.00 eq.) and Methyl-4-chloro-4-oxobutyrate (5.38 g, 0.036 mol, 1.43 eq.) were deployed.

Yield: 5.01 g (66%), yellow oil.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.01 (dq, J = 2.0, 1.0 Hz, 1H<sub>a</sub>), 5.67 (p, J = 1.6 Hz, 1H<sub>b</sub>), 4.08 (t, J = 6.5 Hz, 2H<sub>c</sub>), 4.00 (t, J = 6.5 Hz, 2H<sub>d</sub>), 3.59 (s, 3H<sub>e</sub>), 2.55 (s, 4H<sub>f</sub>), 1.87 (dd, J = 1.6, 1.0 Hz, 3H<sub>g</sub>), 1.68 – 1.51 (m, 4H<sub>h</sub>), 1.33 (p, J = 4.4, 3.6 Hz, 4H<sub>i</sub>).

**Synthesis of Poly[6-(methacryloyloxy)hexyl methyl succinate] PMA6.2.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 6-(methacryloyloxy)hexyl methyl succinate MA6.2 (4.450 g, 14.8 mmol, 1.00 eq.) and AIBN (0.024 g, 0.15 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (20 g) to adjust a monomer-concentration of ca. 20 wt%. After 24 h, ca. 82% conversion was obtained. The polymer was purified by precipitation in MeOH.

Yield: 3.17 g (71 %); clear, amorphous yellow/brown viscous polymer

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.00 (s, 2H<sub>a</sub>), 3.88 (s, 2H<sub>b</sub>), 3.58 (s, 3H<sub>c</sub>), 2.54 (s, 4H<sub>d</sub>), 1.56 (s, 4H<sub>e</sub>), 1.33 (s, 4H<sub>f</sub>), 1.04 – 0.56 (m, 5H<sub>g</sub>).

SEC:  $M_n$  = 49300 g mol<sup>-1</sup>,  $M_p$  = 78200 g mol<sup>-1</sup>, D = 5.21. DSC:  $T_g$  = -44 °C, no  $T_m$ TGA:  $T_{5\%}$  = 289 °C



Figure S1b. <sup>1</sup>H NMR spectra of 6HHM (top), MA6.2 (middle) and PMA6.2 (bottom) including integrals and peak assignments.

## SI 1.6. 2-(methacryloyloxy)ethyl methyl oxalate MA2.0 & Poly[2-(methacryloyloxy)ethyl methyl oxalate] PMA2.0

**Synthesis of 2-(methacryloyloxy)ethyl methyl oxalate MA2.0.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 2-hydroxyethyl methacrylate (HEMA; 10.040 g, 0.077 mol, 1.00 eq.), Triethylamine (15.34 g, 0.152 mol, 1.97 eq.) and Methyl-2-chloro-2-oxoacetate (12.250 g, 0.100 mol, 1.30 eq.) were deployed. In the washing steps during workup, the product was dissolved in Et<sub>2</sub>O instead of DCM.

Yield: 15.47 g (93%), pale-yellow liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.03 (dt, J = 2.0, 1.0 Hz, 1H<sub>a</sub>), 5.69 (h, J = 1.6 Hz, 1H<sub>b</sub>), 4.57 – 4.46 (m, 2H<sub>c</sub>), 4.41 – 4.32 (m, 2H<sub>d</sub>), 3.82 (s, 3H<sub>e</sub>), 1.87 (dd, J = 1.6, 1.0 Hz, 3H<sub>f</sub>).

**Synthesis of Poly[2-(methacryloyloxy)ethyl methyl oxalate] PMA2.0.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 2-(methacryloyloxy)ethyl methyl oxalate MA2.0 (15.211 g, 70.4 mmol, 1.00 eq.) and AIBN (0.116 g, 0.71 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (125 g) to adjust a monomer-concentration of ca. 10 wt%. After 24 h, ca. 88% conversion was obtained. The polymer was purified by precipitation in *n*-Hexane.

Yield: 11.53 g (76 %); clear, amorphous yellow rigid polymer

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.03 (dt, J = 2.0, 1.0 Hz, 1H<sub>a</sub>), 5.69 (h, J = 1.6 Hz, 1H<sub>b</sub>), 4.57 – 4.46 (m, 2H<sub>c</sub>), 4.41 – 4.32 (m, 2H<sub>d</sub>), 3.82 (s, 3H<sub>e</sub>), 1.87 (dd, J = 1.6, 1.0 Hz, 3H<sub>f</sub>). SEC:  $M_n$  = 15600 g mol<sup>-1</sup>,  $M_p$  = 27100 g mol<sup>-1</sup>, D = 2.12. DSC:  $T_g$  = 32 °C, no  $T_m$ TGA:  $T_{5\%}$  = 224 °C



Figure S1c. <sup>1</sup>H NMR spectra of MA2.0 (top) and PMA2.0 (bottom) including integrals and peak assignments.

## SI 1.7. 2-(methacryloyloxy)ethyl methyl malonate MA2.1 & Poly[2-(methacryloyloxy)ethyl methyl malonate] PMA2.1

**Synthesis of 2-(methacryloyloxy)ethyl methyl malonate MA2.1.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 2-hydroxyethyl methacrylate (HEMA; 10.010 g, 0.077 mol, 1.00 eq.), Triethylamine (15.07 g, 0.149 mol, 1.94 eq.) and Methyl-3-chloro-3-oxopropionate (12.270 g, 0.090 mol, 1.17 eq.) were deployed. In the washing steps during workup, the product was dissolved in Et<sub>2</sub>O instead of DCM.

Yield: 13.92 g (79%), pale-yellow liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.04 (dq, J = 1.9, 1.0 Hz, 1H<sub>a</sub>), 5.71 (p, J = 1.6 Hz, 1H<sub>b</sub>), 4.40 – 4.32 (m, 2H<sub>c</sub>), 4.32 – 4.26 (m, 2H<sub>d</sub>), 3.63 (s, 3H<sub>e</sub>), 3.55 (s, 2H<sub>f</sub>), 1.88 (dd, J = 1.6, 1.0 Hz, 3H<sub>g</sub>).

**Synthesis of Poly[2-(methacryloyloxy)ethyl methyl malonate] PMA2.1.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 2-(methacryloyloxy)ethyl methyl malonate MA2.1 (13.920 g, 60.5 mmol, 1.00 eq.) and AIBN (0.100 g, 0.61 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (130 g) to adjust a monomer-concentration of ca. 10 wt%. After 24 h, ca. 87% conversion was obtained. The polymer was purified by precipitation in *n*-Hexane.

Yield: 10.75 g (77 %); clear, amorphous yellow/brown rigid polymer

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.30 (s, 2H<sub>a</sub>), 4.11 (s, 2H<sub>b</sub>), 3.67 (d, J = 2.1 Hz, 3H<sub>c</sub>), 3.59 – 3.48 (m, 2H<sub>d</sub>), 2.10 – 1.58 (m, 3H<sub>e</sub>), 0.85 (d, J = 53.3 Hz, 2H<sub>f</sub>).

SEC:  $M_{\rm n}$  = 16500 g mol<sup>-1</sup>,  $M_{\rm p}$  = 35400 g mol<sup>-1</sup>, D = 2.83.

DSC:  $T_{\rm g}$  = 0 °C, no  $T_{\rm m}$ 

TGA: *T*<sub>5%</sub> = 228 °C



Figure S1d. <sup>1</sup>H NMR spectra of MA2.1 (top) and PMA2.1 (bottom) including integrals and peak assignments.

### SI 1.8. 2-(methacryloyloxy)ethyl methyl succinate MA2.2 & Poly[2-(methacryloyloxy)ethyl methyl succinate] PMA2.2

**Synthesis of 2-(methacryloyloxy)ethyl methyl succinate MA2.2.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 2-Hydroxyethyl methacrylate (HEMA; 10.030 g, 0.077 mol, 1.00 eq.), Triethylamine (16.00 g, 0.158 mol, 2.05 eq.) and Methyl-4-chloro-4-oxobutyrate (15.200 g, 0.101 mol, 1.31 eq.) were deployed. In the washing steps during workup, the product was dissolved in Et<sub>2</sub>O instead of DCM.

Yield: 15.27 g (81%), pale-yellow liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.03 (dq, J = 2.1, 1.0 Hz, 1H<sub>a</sub>), 5.70 (dq, J = 1.6 Hz, 1H<sub>b</sub>), 4.28 (s, 4H<sub>c</sub>), 3.58 (s, 3H<sub>d</sub>), 2.62 - 2.53 (m, 4H<sub>e</sub>), 1.88 (dd, J = 1.6, 1.0 Hz, 3H<sub>f</sub>).

**Synthesis of Poly[2-(methacryloyloxy)ethyl methyl succinate] PMA2.2.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 2-(methacryloyloxy)ethyl methyl succinate MA2.2 (15.270 g, 62.5 mmol, 1.00 eq.) and AIBN (0.102 g, 0.62 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (120 g) to adjust a monomer-concentration of ca. 10 wt%. After 24 h, ca. 85% conversion was obtained. The polymer was purified by precipitation in *n*-Hexane.

Yield: 11.15 g (73 %); clear, amorphous yellow/brown viscous polymer

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.23 (s, 2H<sub>a</sub>), 4.09 (s, 2H<sub>b</sub>), 3.60 (s, 3H<sub>c</sub>), 2.58 (s, 4H<sub>d</sub>), 1.77 (s, 3H<sub>e</sub>), 0.86 (d, J = 53.3 Hz, 2H<sub>f</sub>).

SEC:  $M_n$  = 19100 g mol<sup>-1</sup>,  $M_p$  = 35100 g mol<sup>-1</sup>, D = 2.62. DSC:  $T_g$  = -7 °C, no  $T_m$ TGA:  $T_{5\%}$  = 262 °C



Figure S1e. <sup>1</sup>H NMR spectra of MA2.2 (top) and PMA2.2 (bottom) including integrals and peak assignments.

# SI 1.9. 4-(acryloyloxy)butyl methyl succinate A4.2 & Poly[4-(acryloyloxy)butyl methyl succinate] PA4.2

**Synthesis of 4-(acryloyloxy)butyl methyl succinate A4.2.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 4-Hydroxybutylacrylate (11.530 g, 0.080 mol, 1.00 eq.), Pyridine (12.74 g, 0.161 mol, 2.01 eq.) and Methyl-4-chloro-4-oxobutyrate (14.520 g, 0.096 mol, 1.21 eq.) were deployed. In the washing steps during workup, the product was dissolved in Et<sub>2</sub>O instead of DCM.

Yield: 13.15 g (64%), clear colorless liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.33 (dd, J = 17.3, 1.8 Hz, 1H<sub>a</sub>), 6.17 (dd, J = 17.2, 10.1 Hz, 1H<sub>b</sub>), 5.94 (dd, J = 10.2, 1.8 Hz, 1H<sub>c</sub>), 4.11 (t, J = 6.0 Hz, 2H<sub>d</sub>), 4.04 (t, J = 6.0 Hz, 2H<sub>e</sub>), 3.59 (s, 3H<sub>f</sub>), 2.55 (s, 4H<sub>g</sub>), 1.64 (hept, J = 2.9 Hz, 4H<sub>h</sub>).

**Synthesis of Poly[4-(acryloyloxy)butyl methyl succinate] PA4.2.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 4-(acryloyloxy)butyl methyl succinate A4.2 (13.150 g, 50.9 mmol, 1.00 eq.) and AIBN (0.084 g, 0.51 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (15 g) to adjust a monomer-concentration of ca. 50 wt%. After 24 h, full conversion (>99%) was obtained. The polymer was purified by precipitation in  $Et_2O$  and *n*-Hexane.

Yield: 12.36 g (94 %); clear, amorphous colorless low-viscous polymer <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.02 (s, 4H<sub>a</sub>), 3.58 (s, 3H<sub>b</sub>), 2.54 (s, 4H<sub>c</sub>), 1.60 (s, 4H<sub>d</sub>). SEC:  $M_n$  = 96800 g mol<sup>-1</sup>,  $M_p$  = 144100 g mol<sup>-1</sup>, D = 2.71. DSC:  $T_g$  = -42 °C, no  $T_m$ TGA:  $T_{5\%}$  = 349 °C



Figure S1f. <sup>1</sup>H NMR spectra of A4.2 (top) and PA4.2 (bottom) including integrals and peak assignments.

## SI 1.10. 4-(acryloyloxy)butyl methyl adipate A4.4 & Poly[4-(acryloyloxy)butyl methyl adipate] PA4.4

**Synthesis of 4-(acryloyloxy)butyl methyl adipate A4.4.** The synthesis was performed in analogy to the general procedure of the esterification of an acyl chloride and an alcohol described in the main article. Therefore, 4-Hydroxybutylacrylate (13.603 g, 0.094 mol, 1.00 eq.), Pyridine (15.64 g, 0.198 mol, 2.10 eq.) and Methyl-6-chloro-6-

oxohexanoate (Methyladipoylchloride; 19.310 g, 0.108 mol, 1.15 eq.) were deployed. In the washing steps during workup, the product was dissolved in  $Et_2O$  instead of DCM.

Yield: 24.31 g (90%), clear colorless liquid.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.33 (dd, J = 17.2, 1.8 Hz, 1H<sub>a</sub>), 6.17 (dd, J = 17.2, 10.2 Hz, 1H<sub>b</sub>), 5.94 (dd, J = 10.2, 1.8 Hz, 1H<sub>c</sub>), 4.11 (t, J = 6.0 Hz, 2H<sub>d</sub>), 4.03 (t, J = 6.0 Hz, 2H<sub>e</sub>), 3.58 (s, 3H<sub>f</sub>), 2.37 – 2.22 (m, 4H<sub>g</sub>), 1.73 – 1.58 (m, 4H<sub>h</sub>), 1.56 – 1.44 (m, 4H<sub>i</sub>).

**Synthesis of Poly[4-(acryloyloxy)butyl methyl adipate] PA4.4.** The polymerization was performed in analogy to the general procedure of the free radical polymerization of acrylate and methacrylate monomers described in the main article. Therefore, 4-(acryloyloxy)butyl methyl adipate A4.4 (18.300 g, 63.9 mmol, 1.00 eq.) and AIBN (0.105 g, 0.564 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (275 g) to adjust a monomer-concentration of ca. 5 wt%. After 24 h, ca. 93% conversion was obtained. The polymer was purified by precipitation in *n*-Hexane and MeOH.

Yield: 15.92 g (87 %); clear, amorphous colorless very-low-viscous polymer <sup>1</sup>H NMR (300 MHz, DMSO-*d* <sub>6</sub>)  $\delta$  4.00 (s, 4H<sub>a</sub>), 3.56 (s, 3H<sub>b</sub>), 2.28 (s, 4H<sub>c</sub>), 1.55 (s, 8H<sub>d,e</sub>). SEC:  $M_n$  = 6900 g mol<sup>-1</sup>,  $M_p$  = 7600 g mol<sup>-1</sup>, D = 2.52. DSC:  $T_g$  = -58 °C, no  $T_m$ TGA:  $T_{5\%}$  = 362°C



Figure S1g. <sup>1</sup>H NMR spectra of A4.4 (top) and PA4.4 (bottom) including integrals and peak assignments.

#### SI 1.11. Poly(butylacrylate) PBA1 & PBA2

**Synthesis of Poly(butylacrylate) 1 PBA1.** The polymerization was performed in analogy to the above described general procedure of the free radical polymerization of acrylate and methacrylate monomers. Therefore, butylacrylate (15.030 g, 117.3 mmol, 1.00 eq.) and AIBN (0.192 g, 1.17 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (150 g) to adjust a monomer-concentration of ca. 9 wt%. After 24 h, full conversion was obtained. As no further impurities could be detected, the product was only dried during workup.

Yield: 15.01 g (>99 %); clear, amorphous colorless low-viscous polymer

<sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  4.04 (t, 2H<sub>a</sub>), 2.29 (s, 1H<sub>b</sub>), 1.90 (s, 1H<sub>c</sub>), 1.60 (p, *J* = 7.1 Hz, 3H<sub>d+e</sub>), 1.38 (h, *J* = 7.2 Hz, 2H<sub>f</sub>), 0.95 (t, *J* = 7.3 Hz, 3H<sub>g</sub>).

SEC:  $M_n = 10700 \text{ g mol}^{-1}$ ,  $M_p = 34500 \text{ g mol}^{-1}$ , D = 3.19. DSC:  $T_g = -50 \text{ °C}$ , no  $T_m$ TGA:  $T_{5\%} = 295 \text{ °C}$ 

**Synthesis of Poly(butylacrylate) 2 PBA2.** The polymerization was performed in analogy to the above described general procedure of the free radical polymerization of acrylate and methacrylate monomers. Therefore, butylacrylate (15.080 g, 117.7 mmol, 1.00 eq.) and AIBN (0.191 g, 1.17 mmol, 0.01 eq.) were deployed. The reactants were dissolved in 1,4-Dioxan (75 g) to adjust a monomer-concentration of ca. 17 wt%. After 24 h, full conversion was obtained. As no further impurities could be detected, the product was only dried during workup.

Yield: 15.04 g (>99 %); clear, amorphous colorless low-viscous polymer

<sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  4.16 – 3.91 (t, 2H<sub>a</sub>), 2.27 (s, 1H<sub>b</sub>), 1.90 (s, 1H<sub>c</sub>), 1.59 (p, *J* = 7.2 Hz, 3H<sub>d+e</sub>), 1.36 (h, *J* = 7.6 Hz, 2H<sub>f</sub>), 0.93 (t, *J* = 7.4 Hz, 3H<sub>g</sub>).

SEC:  $M_n$  = 21500 g mol<sup>-1</sup>,  $M_p$  = 69900 g mol<sup>-1</sup>, D = 4.17.

DSC:  $T_g = -50$  °C, no  $T_m$ 

TGA: *T*<sub>5%</sub> = 295 °C



Figure S1h. <sup>1</sup>H NMR spectra of PBA1 (top) and PBA2 (bottom) including integrals and peak assignments.

#### SI 2. Electrochemical Measurements

#### SI 2.1. Preparation of Solid Polymer Electrolytes (SPE)

The respective amounts of polymer and salt were weighed out separately and dissolved each in a small amount of dry acetonitrile. In the case of LiTFSI, this was carried out quickly under air, while for the highly hygroscopic LiFSI the procedure was performed under argon in an inert glovebox atmosphere.

- For pristine SPE, both solutions were then mixed in small sample vials and the solvent was removed under stirring on a hotplate (70 °C).
- In the case of TiO<sub>2</sub> nanoparticles (P25) ceramic-in-polymer SPEs, a corresponding amount of 10 wt% of the nanopowder was weighed out and dispersed in dry acetonitrile (ca. 150 mg P25 to ca. 5 mL CH<sub>3</sub>CN) using an ultrasonicator for ca. 2h. The solutions of polymer and lithium salt (summing up to the remaining 90 wt%) were slowly added to the P25 dispersion under stirring. Consequently, the solvent was removed on a hotplate (70 °C) until a highly viscous mass was obtained (in the case of LiFSI this was performed inside the glovebox).

In the case of the LiFSI mixtures, a custom-made glass evacuation chamber on top of the stirrer was used for solventremoval inside the glovebox. All samples were finally dried in a drying oven outside the glovebox at at least 80 °C in high vacuum for at least one day and after that stored in the glovebox until electrochemical test cells were fabricated.

#### SI 2.2. Electrochemical Characterization

All electrochemical experiments were carried out on a BioLogic VMP-300 potentiostat using the measurement software EC-Lab V11.26. All impedance spectra measured during this study were reconstructed with extended Distribution of Relaxation Times (eDRT) using the software ec–idea, which is described elsewhere.<sup>[3,4]</sup> Fitting parameters: Number of time constants: 159, 3-fold number of measured frequencies, extended upper time constant limit by 1 decade, extended lower time constant limit by 1 decade, Regularization parameter: 0.1.

The temperature-dependent measurements were performed inside a Vötsch VT 4002 temperature chamber. All preparations and cell fabrication were conducted in an argon-filled inert glovebox utilizing a copper catalyst for gas purification ( $H_2O < 0.1$  ppm and  $O_2 < 1$  ppm).

#### SI 2.3. Ionic Conductivity

The ionic conductivities of all SPES were determined by electrochemical impedance spectroscopy (EIS) in the frequency range of 3 MHz to 1Hz with a sinusoidal amplitude of 20 mV. Therefore, the electrolytes were sandwiched between stainless-steel electrodes (StSt|SPE|StSt). The temperature-dependent impedance was recorded at temperatures ranging from 80 °C to 25 °C and the ionic conductivity values ( $\sigma$ ) were calculated from the bulk resistance of the electrolyte ( $R_{\Omega}$ ), thickness of the electrolyte (I) and the area of the electrode (A) at each temperature as follows:

$$\sigma = \frac{l}{R_{\Omega}A}$$
 (formula S3)

The ionic conductivity values in the Arrhenius plots were fitted by a VTF fit:

$$\sigma = \frac{A}{\sqrt{T}} \cdot exp^{(\frac{-E_a}{R(T-T_0)})}$$
(formula S4)

Where A is a pre-exponential factor, B describes the pseudo-activation energy and  $T_0$  is the zero-mobility temperature.<sup>[5,6]</sup>

#### SI 2.4. Electrochemical stability (LSV)

The electrochemical stability was examined using linear sweep voltammetry at 70 °C. Therefore, CR2032 coin cells with an asymmetric two-electrode setup (StSt|SPE|Li) were assembled. The stainless-steel plate acts as working electrode and the Li metal foil as counter and reference electrode. During the measurement, the potential is swept from 0 to 6 V vs. Li/Li<sup>+</sup> at a constant scan rate of 0.1 mV s<sup>-1</sup>.

#### SI 2.5. Fabrication of the symmetric Li|SPE|Li cells

Outside of the glovebox, discs of 14 mm diameter were punched out of a porous 8 µm track-etched PI membrane (19 % porosity) and clamped within a self-made holder providing free access to both sides. The membrane was soaked and impregnated on both sides with a solution of the SPE in acetonitrile and then put into a vacuum drying furnace (still inside the holder) where it was dried over night at 80 °C. The dried disc was then transferred into the glovebox and sandwiched between two discs of lithium metal foil (thickness: 380 µm, diameter: 14 mm). Finally, the coin cell is assembled and sealed.

#### SI 2.6. Lithium-ion Transport Number (t<sub>Li+</sub>)

The lithium-ion transport number  $(t_{Li+})$  of the electrolytes was studied using a combination of EIS and chronoamperometry (CA) in symmetric lithium cells (Li|SPE|Li), referred to as the Bruce and Vincent method.<sup>[7]</sup> Prior to the measurements the cells were stabilized for 12 h at 70 °C to optimize the contact between the electrode and the electrolyte. Thereafter, impedance spectra were recorded in the frequency range of 3 MHz to 0.1 Hz with a sinusoidal amplitude of 20 mV, followed by a CA interval applying a DC potential of  $E_i = 50$  mV until steady-state current was obtained. After the DC polarization, another impedance spectrum was recorded. The lithium-ion transport number was then calculated according to the following formula:

$$t_{Li}^{} + = \frac{I_{ss}(\Delta V - I_0 R_{i,0})}{I_0(\Delta V - I_{ss} R_{i,ss})}$$
(formula S5)

Where  $I_0$  and  $I_{ss}$  are the initial and steady-state currents, respectively, within the CA step, while  $\Delta V$  is the applied potential.  $R_{i,0}$  and  $R_{i,ss}$  are the initial and steady-state interfacial resistances calculated from the impedance spectra of the cell before and after polarization.

#### SI 2.7. Galvanostatic Cycling / Lithium Plating and Stripping

Lithium plating and stripping was investigated by galvanostatic cycling of symmetric Li|SPE|Li cells with a constant current density of 0.53 mA cm<sup>-2</sup> at 70 °C and at 40 °C. The duration of each cycle was 2 h (1h each for charge/discharge, respectively). After every 25 cycles at 70 °C and after every 20 cycles at 40 °C, the impedance was measured to analyze the interfacial resistance.

#### SI 2.8. Preparation of the LiFePO<sub>4</sub> (LFP) cathodes and battery cells

The electrode was prepared using

- standard LFP as the active material,
- super P carbon and conductive graphite as the electron conducting medium and
- Polyvinylidene fluoride (PVDF; in LFP1), PA4.4 (in LFP2) or PA4.4+ PVDF (in LFP3) as the ion conducting matrix.

The cathode mixtures were prepared using acetonitrile (CH<sub>3</sub>CN) and *N*-Methyl-2-pyrrolidone (NMP) as solvents. The weight proportions of all components are displayed in Table S2. The mixtures were ball milled for 2 h to get homogenous slurries and subsequently cast onto a carbon-coated aluminium current collector by doctor blading. The resulting electrode film was dried *in vacuo* overnight at 80 °C. After cooling down to room temperature, the electrodes were densified by a calendering process, punched into discs of 14 mm diameter by a disc cutter and then applied in the cell fabrication. The absolute mass of active material (LFP) loading in the cathodes is also provided in the Table S2.

Table S2. Cathode compositions of LFP1, LFP2 and LFP3 comprising components and composition, calendering procedure, solvents and absolute LFP mass loading.

components		composition	calondoring	CH <sub>3</sub> CN + NMP	LFP loading
		composition	calendering	(mL)	(mg)
LFP1	LFP CB CG PVDF	80 7 3 10	yes	3.5	3.7
LFP2	LFP CB CG PA4.4 LiFSI	63 4.9 2.1 7.5 22.5	no	3 + 0.5	5.2
LFP3	LFP CB CG PA4.4 PVDF LiFSI	63 4.9 2.1 5.25 9 15.75	yes	2 + 1.5	4.0

Outside of the glovebox, discs of 14 mm diameter were punched out of a porous 8 µm track-etched PI membrane (19 % porosity), placed on a glass slide and heated to 100 °C on a hot plate. Meanwhile, a 14 mm cathode (prepared as described above) was placed in the bottom part of a CR2032 coin cell. The heated PI membrane is then soaked with a thin layer of the PA4-25F-NP SPE dissolved in acetonitrile, after which the solvent is partly removed for ca. 2 minutes. The porous membrane is then placed onto the cathode facing it with the electrode-coated side. Care is taken to avoid solvent reaching the cathode slurry. After the coin cell is placed onto the hot plate, the now top (uncoated) side of the PI membrane is then also impregnated with electrolyte solution. This half cell setup is placed in the vacuum oven over night at 80 °C to remove all acetonitrile traces. After that, it is transferred into the glovebox, where a disc of lithium metal foil (thickness: 380 µm, diameter: 14 mm) is placed on top of the membrane. Finally, the coin cell is assembled and sealed.

#### SI 2.9. Battery cell cycling

Galvanostatic cycling of the assembled battery cells was performed between 2.5 and 4.2 V in different experiments: Rate capability performance tests were carried out using cells with LFP1, LFP2 and LFP3 cathodes at 70 °C for Crates of 0.2, 0.5, 1.0, 2.0, 1.0, 0.5 and 0.2 in this order (5 cycles each). Long-term cycling was performed using cells with LFP1, LFP2 and LFP3 cathodes at 70 °C and 1C for 100 cycles and additionally with LFP3 cells at 70 °C and 2C for 300 cycles. Moreover, long-term cycling using cells with a LFP3 cathode was performed at 40 °C and 0.1C for 50 cycles.

Table S3. Initial discharge capacities of the Li| PA4.4-25F-NP|LFP<sub>x</sub> battery cells with three different cathode compositions (LFP1, LFP2, LFP3) at various C-rates.

C rate	LFP1	LFP2	LFP3	
	(mAh g <sup>-1</sup> )	(mAh g <sup>-1</sup> )	(mAh g⁻¹)	
0.2	143	145	152	
0.5	121	122	136	
1	91	101	118	
2	66	76	105	
0.2	134	132	144	



Figure S3. SEC curves (eluent: THF + 0.25 wt% TBAB, PS standard) of a) all (meth)acrylate diester polymers synthesized in this work and b) PBA1 and PBA2 reference polymers.

#### SI 3. SEC



![](_page_17_Figure_1.jpeg)

Figure S4. DSC curves ( $2^{nd}$  heating and cooling, 10 K min<sup>-1</sup>) of a) PMA2.0 and PMA 2.0-25T, b) PMA2.1 and PMA2.1-25T, c) PMA2.2 and PMA2.2-25T, d) PMA4.2, PMA 4.2-10T and PMA4.2-25T, e) PMA4.2-50T, PMA4.2-70T and PMA4.2-80T, f) PMA6.2 and

PMA6.2-25T, g) PA4.2, PA4.2-25T and PA4.2-25T-NP, h) PA4.4 and PA4.4-25T, i) PCI and PCI-25T and j) PA4.2-25F-NP and PA4.4-25F-NP.

![](_page_19_Figure_0.jpeg)

![](_page_19_Figure_1.jpeg)

T/°C

Figure S5. TGA curves of a) all methacrylate-based diester polymers and b) all acrylate based diester polymers (including reference polymers PBA1 + PBA2) synthesized in this study.

![](_page_20_Figure_0.jpeg)

Figure S6. Arrhenius-plots of the ionic conductivity and corresponding VTF fits of a) PMA4.2 SPEs with different amounts of LiTFSI salt (10, 25, 50, 70 and 80 wt%, screening of salt concentration), b) PMA2.0-25T, PMA2.1-25T and PMA2.2-25T (screening of the diester spacer length y), c) PMA2.2-25T, PMA4.2-25T and PMA6.2-25T (screening of the spacer length x between polymer backbone and diester group), d) PA4.2-25T and PMA4.2-25T (methacrylate vs. acrylate backbone), e) PA4.2-25T and PA4.2-25T (influence of the TiO<sub>2</sub> nanoparticles), f) PA4.2-25T and PA4.4-25T (influence of additional *T*<sub>g</sub> decrease by larger diester spacer), g) comparison of the highest-conducting diester in this study PA4.4-25T with the reference SPEs PCI-25T and PBA1-25T and h) PA4.2-25F-NP and PA4.4-25F-NP (LiFSI instead of LiTFSI).

![](_page_21_Figure_0.jpeg)

Figure S7. Values of the Ionic conductivity as VTF plots including their VTF fits for a) PMA4.2 SPEs with 10, 25, 50, 70 and 80 wt% LiTFSI, b) PMA2.0-25T, PMA2.1-25T, PMA2.2-25T, PMA6.2-25T, c) PA4.2-25T, PA4.2-25T-NP, PA4.4-25T, PBA1-25T and d) PA4.2-25F-NP and PA4.4-25F-NP.

Table S4. Slo	oe and activation	energies $E_{2}$	derived from the	VTF fits	displayed in	Figure S7 f	or all p	olymers m	easured in	this work
1 4 5 1 5 1 5 10	oc ana activation	Chergies La		• • • • • • • •	alsplayeam		or an p	ory mension	cusurcu m	

Electrolyte	Slope / K	$E_{a}/kJ mol^{-1}$
PMA4.2-10T	1286.5	10.7
PMA4.2-25T	1220.4	10.1
PMA4.2-50T	1195	9.9
PMA4.2-70T	1092.4	9.1
PMA4.2-80T	1472.1	12.2
PMA2.0-25T	873.23	7.3
PMA2.1-25T	923.26	7.7
PMA2.2-25T	1338.9	11.1
PMA6.2-25T	1302.5	10.8
PA4.2-25T	1249.1	10.4
PA4.2-25T- NP	1230.6	10.2
PA4.4-25T	1221.5	10.2
PBA1-25T	996.16	8.3

### SI 8. Lithium Transport Number

![](_page_22_Figure_1.jpeg)

PA4.2-25F-NP

t / min

• 10 mV

150 200

60

50-

₹40-30-

20-

10-

0 50 100

![](_page_22_Figure_2.jpeg)

![](_page_23_Figure_0.jpeg)

![](_page_23_Figure_1.jpeg)

Figure S8. Nyquist plots (squares are measured points) and the corresponding eDRT fits (solid lines) of EIS measurements using symmetrical Li|SPE|Li cells, measured before and after chronoamperometrical polarization at 10 mV and 70 °C for the determination of the lithium transport number  $t_{\text{Li+}}$  (inset: current vs. time during the CA polarization) for a) PCI-25T, b) PMA4.2-25T, c) PA4.2-25T, d) PA4.2-25T-NP, e) PA4.2-25F-NP and f) PA4.4-25F-NP. The value of  $t_{\text{Li+}}$  determined by the method after Bruce and Vincent is displayed.

![](_page_24_Figure_0.jpeg)

![](_page_24_Figure_1.jpeg)

![](_page_24_Figure_2.jpeg)

![](_page_24_Figure_3.jpeg)

![](_page_24_Figure_4.jpeg)

the cell as well as the corresponding e-DRT plots for a/b) PA4.2-25T, c/d) PA4.2-25T-NP, e/f) PA4.2-25F-NP and g/h) PA4.4-25F-NP.

![](_page_26_Figure_0.jpeg)

SI 10. Linear sweep voltammetry (LSV)

Figure S10. (a) Linear Sweep Voltammetry profiles (0-6 V vs. Li/Li<sup>+</sup>) of PA4.4-25T, PMA4.2-25T and PCI-25T SPEs. (b) Magnified LSV profiles of (a).

- [1] H. Beyer, W. Walter, Lehrbuch der organischen Chemie: Mit 20 Tabellen, Hirzel, Stuttgart 1984.
- [2] S. Hauptmann, *Organische Chemie*, Dt. Verl. für Grundstoffindustrie; Wiley-VCH, Leipzig, Weinheim **2001**.
- [3] M. Hahn, S. Schindler, L.-C. Triebs, M. A. Danzer, *Batteries* **2019**, *5*, 43, DOI: 10.3390/batteries5020043.
- [4] M. Hahn, D. Rosenbach, A. Krimalowski, T. Nazarenus, R. Moos, M. Thelakkat, M. A. Danzer, *Electrochimica Acta* **2020**, *344*, 136060, DOI: 10.1016/j.electacta.2020.136060.
- [5] N. A. Stolwijk, M. Wiencierz, C. Heddier, J. Kösters, J. Phys. Chem. B 2012, 116, 3065, DOI: 10.1021/jp2111956.
- K. M. Diederichsen, H. G. Buss, B. D. McCloskey, *Macromolecules* 2017, 50, 3831, DOI: 10.1021/acs.macromol.7b00423.
- [7] J. Evans, C. A. Vincent, P. G. Bruce, *Polymer* 1987, 28, 2324, DOI: 10.1016/0032-3861(87)90394-6.