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From Plastic Waste to Polymer Electrolytes for Batteries through Chemical Upcycling of Polycarbonate

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1. General information

Materials

Bisphenol A based polycarbonate (BPA-PC) was purchased from from Idemitsu Chemical Europe (TARFLON IV1900R), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and methane sulfonic acid (MSA) were purchased from Sigma-Aldrich. 1,3-propanediol, 1,4-buatanediol, 1,5-pentanediol, Dry dimethyl carbonate (DMC) (99+%) and 4-dimethylaminopyridine (DMAP) (99%) were purchased from Across Orgaics. DMAP was dried applying vacuum for 4 h at room temperature before using. Lithium bis(trifluoromethane)sulfonamide (LiTFSI) was supplied from Solvionic.

Nuclear magnetic resonance (NMR) experiments. ^{1}H and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d_6) on Bruker Advance 300 (300 MHz).

Size Exclusion Chromatography (SEC). SEC was employed to determine molecular weight and molecular weight distributions of polymers. The polymerized materials were dissolved in tetrahydrofuran (THF) (SEC grade) at a concentration of 5 mg mL^{-1} and then filtered with a 0.45 mm nylon filter. The SEC components were three columns in series (Styragel HR2, HR4, and HR6 with pore sizes ranging from 102 to 106 Å), a precision pump (LC-20A, Shimadzu), an autosampler (Waters 717), and a differential refractometer (Waters 2410). The SEC chromatograms were obtained at 35 °C at 1 mL min^{-1}. The curve was calibrated using narrow polystyrene standards, ranging from 595 to 3.95 × 10−6 g mol−1 (fifth order universal calibration).

Differential scanning calorimetry (DSC). Thermal properties were determined with a PerkinElmer 8500 DSC. 5 mg samples were used in an aluminum pan. DSC experiments were carried out in between −70 and 150 °C, and the heating and cooling scans were recorded at 20 °C/min.

Thermogravimetric analysis (TGA)

DSC analysis were performed using TGAQ500 (TA instrument) under nitrogen atmosphere. 5-10 mg of samples were heated from 30 to 800 °C.

Electrochemical characterization. Ionic conductivity (σ) of the polymer electrolytes was measured by AC impedance spectroscopy, range from 100 mHz to 1MHz with an amplitude of 10 mV in a temperature range from 100 °C to 27 °C.

2. Synthetic procedure for the depolymerization of BPA-PC

Reaction 1

In a Schlenk flask, BPA-PC (10 g, 39.3 mmol, 1 eq.), 1,3-propanediol (**3D**; 17.9 g, 235.8 mmol, 6 eq.), TBD (818 mg, 5.89 mmol, 0.15 eq.) and MSA (565 mg, 5.89 mmol, 0.15 eq.) were added in a nitrogen-filled glovebox. The reaction mixture was stirred at 160 °C in an oil bath until complete disappearance of any BPA-PC pellets. After the completion of the reaction, the crude product was cooled to room temperature and analyzed by NMR spectroscopy. . BPA and **3C** were isolated by column chromatography on silica gel using ethyl acetate/hexane as the mobile. ^{1}H NMR (300 MHz, DMSO-d_6) : δ 1.73 (m, 4H, $CH_2C\underline{H_2}CH_2$), 3.44 (m, 4H, $CH_2C\underline{H_2}OH$), 4.12 (t, 4H, $OCOOC\underline{H_2}CH_2$), 4.54 (t, 2H, $CH_2O\underline{H}$)

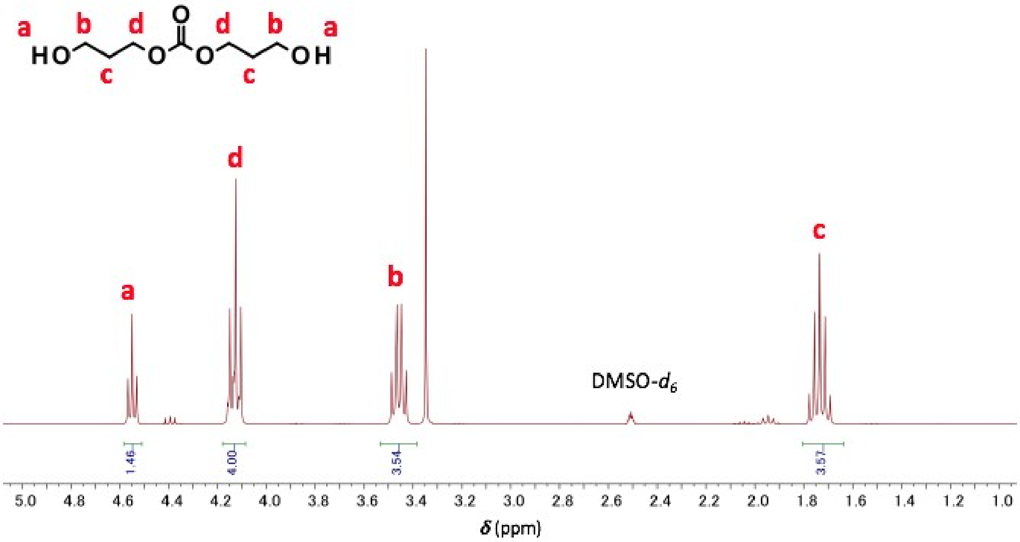

Figure S1. ^{1}H NMR spectrum of **3C** (DMSO-*d*, 300 MHz)

Reaction 2

In a Schlenk flask, BPA-PC (2 g, 7.8 mmol, 1 eq.), 1,4-butanediol (**4D**; 4.21 g, 46.8 mmol, 6 eq), TBD (167 mg, 1.17 mmol, 0.15 eq.) and MSA (115 mg, 1.17 mmol, 0.15 eq.) were added in a nitrogen-filled glovebox. The reaction mixture was stirred at 160 °C in an oil bath until complete disappearance of any BPA-PC pellets. This compound is not isolated.

Reaction 3

In a Schlenk flask, BPA-PC (2 g, 7.8 mmol, 1 eq.), 1,5-pentanediol (**5D**; 4.91 g, 47.2 mmol, 6 eq), TBD (167 mg, 1.17 mmol, 0.15 eq.) and MSA (115 mg, 1.17 mmol, 0.15 eq.) were added in a nitrogen-filled glovebox. The reaction mixture was stirred at 160 °C in an oil bath until complete disappearance of any BPA-PC pellets. After the completion of the reaction, the crude product was cooled to room temperature and analyzed by NMR spectroscopy. BPA and **5C** were isolated by column chromatography on silica gel using ethyl acetate/hexane as the mobile. ^1H NMR (300 MHz, DMSO-d_6): δ 1.23-1.48 (m, 8H, $OCOOCH_2CH_2C\underline{H_2}C\underline{H_2}CH_2CH_2$), 1.58 (m, 4H, $OCOOCH_2C\underline{H_2}CH_2$), 3.39 (t, 4H, $CH_2C\underline{H_2}OH$), 4.05 (t, 4H, $OCOOC\underline{H_2}CH_2$), 4.36 (t, 2H, $CH_2O\underline{H}$)

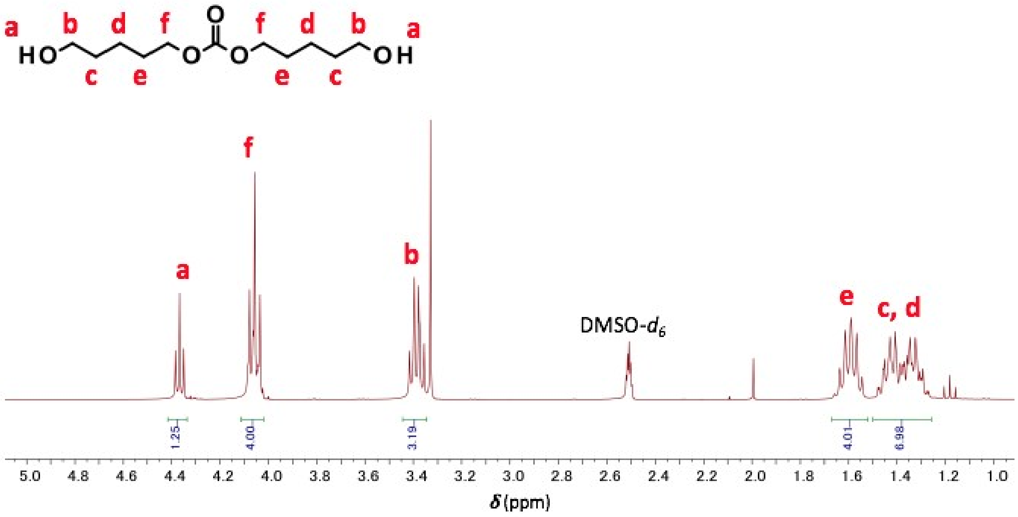

Figure S2. ^1H NMR spectrum of **5C** (DMSO-d_6, 300 MHz).

3. Kinetic study of depolymerization reactions.

Kinetic profiling of depolymerization reactions were analyzed by ^{1}H NMR. The reactions were carried out as mentioned above of session 2. At predetermined time intervals, 0.1 ml aliquots were withdrawn from a reaction in Schlenk flask using a syringe and put into vial. Then 0.6 ml of DMSO-d6 was added. The aliquots were analyzed by ^{1}H NMR for determining the conversion.

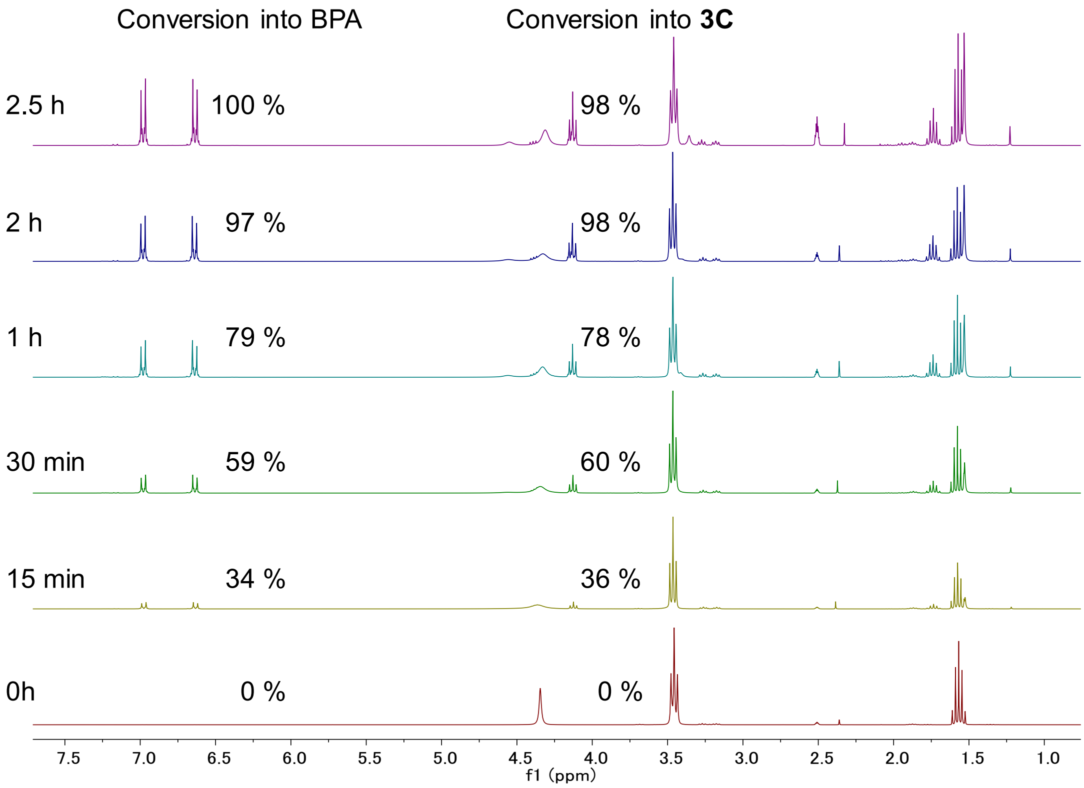

Figure S3. Kinetic study of depolymerization reaction (**1**) into BPA and **3C** analyzed by ^{1}H NMR spectra (DMSO-d_6, 300 MHz).

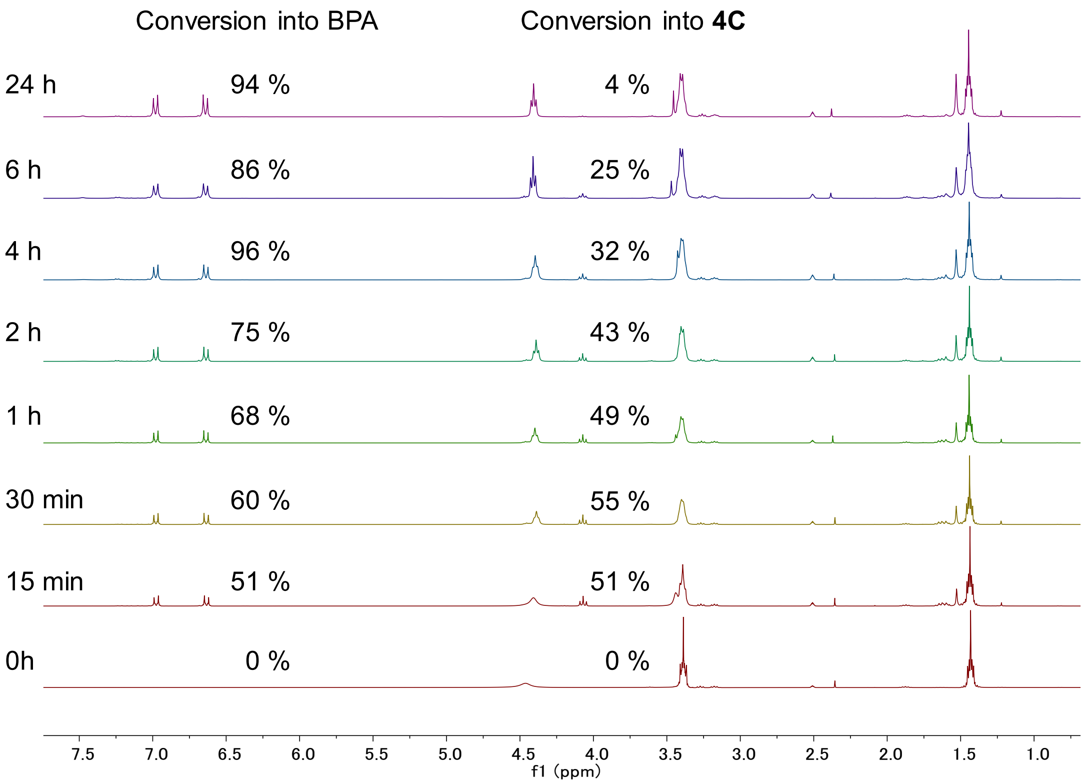

Figure S4. Kinetic study of depolymerization reaction (**2**) into BPA and **4C** analyzed by ^{1}H NMR spectra (DMSO-d_6, 300 MHz).

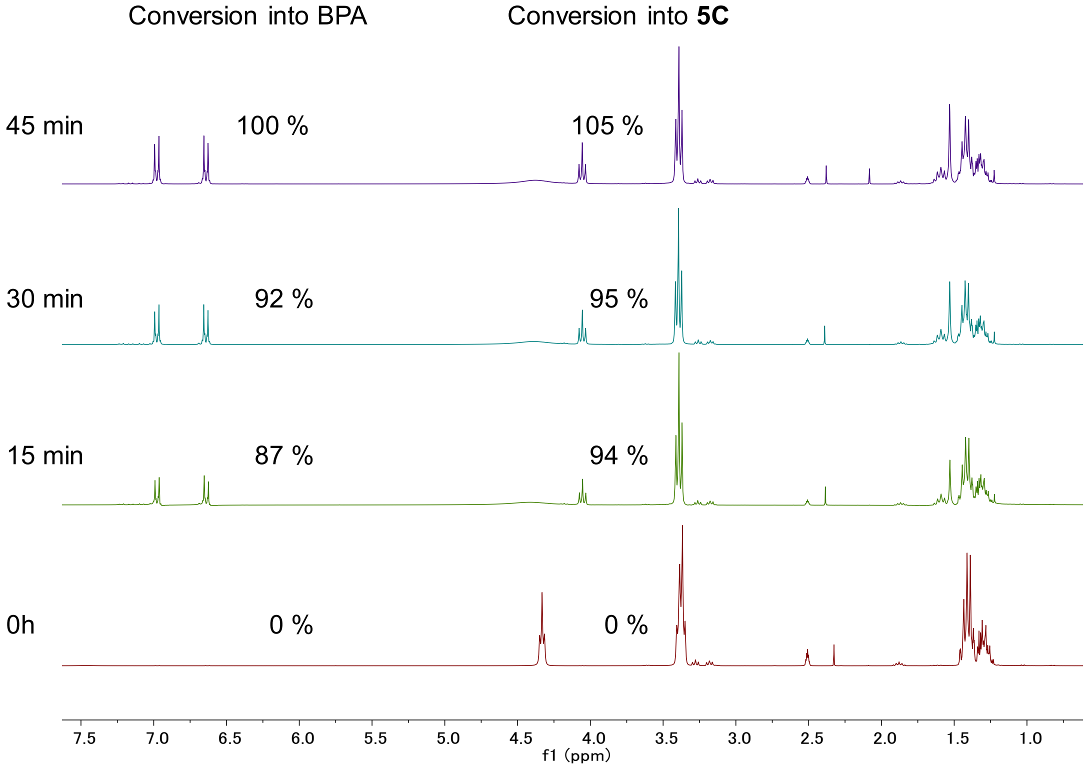

Figure S5. Kinetic study of depolymerization reaction (**3**) into BPA and **5C** analyzed by ^{1}H NMR spectra (DMSO-d_6, 300 MHz).

4. Synthetic procedures for aliphatic polycarbonates

A series of polycarbonate were synthesised by melt polycondensation.

For the synthesis of **P3C**

3C (1.691 g, 9.4 mmol, 1 eq.), DMC (1.71 mg, 18.9 mmol, 2 eq.), DMAP (11.6 mg, 0.094 mmol, 0.01 eq.) were added in a Schlenk flask. The reaction mixture was stirred at 130 °C, 4h in the first step. In the second step, the temperature was increased at 170 °C under high vacuum condition for overnight. After the reaction, the reaction mixture was dissolved in chloroform and precipitated into cold diethyl ether. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.94 (m, $OCOOCH_2C\underline{H_2}CH_2$), 4.13 (t, $OCOOC\underline{H_2}CH_2$), ^{13}C NMR (300 MHz, DMSO-d_6) : δ 27.53, 64.28, 154.44

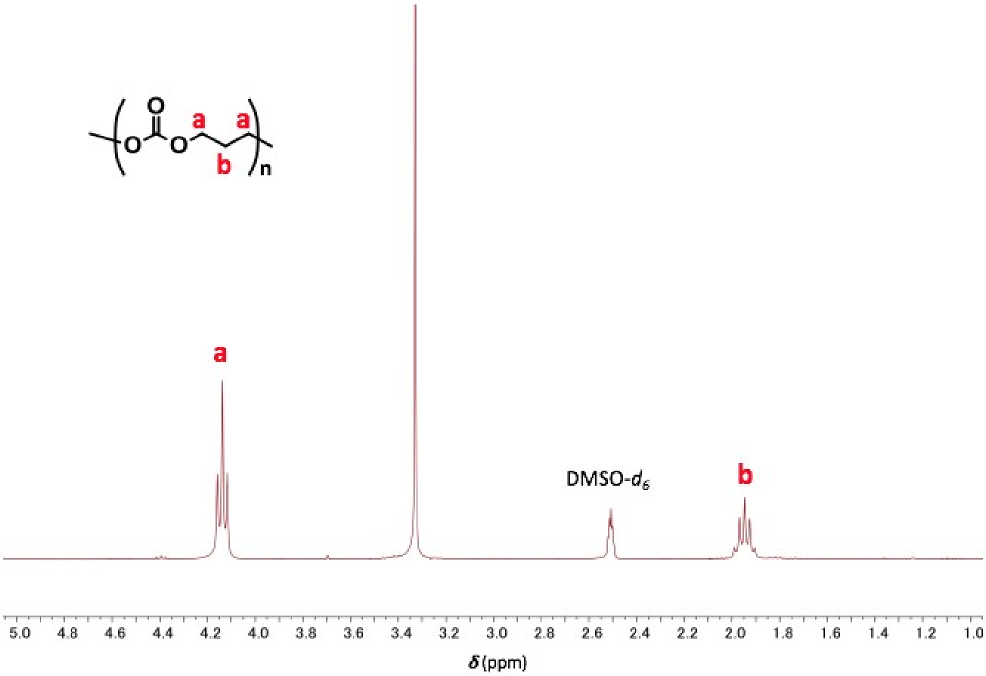

Figure S6. ^{1}H NMR spectrum of **P3C** (DMSO-d_6, 300 MHz).

For the synthesis of **P5C**

5C (1 g, 3.93 mmol, 1 eq.), DMC (0.708 mg, 7.86 mmol, 2 eq.), DMAP (4.8 mg, 0.039 mmol, 0.01 eq.) were added in a Schlenk flask. The reaction mixture was stirred at 130 °C, 4h, then the temperature was increased at 170 °C under high vacuum condition for overnight. After the reaction, the reaction mixture was dissolved in dichloromethane and precipitated into cold methanol. ^{1}H NMR (300 MHz, DMSO-d_6) : δ 1.34 (m, $OCOOCH_2CH_2C\underline{H_2}CH_2$), 1.60 (m, $OCOOCH_2C\underline{H_2}CH_2C\underline{H_2}CH_2$), 4.05 (t, $OCOOC\underline{H_2}CH_2$), ^{13}C NMR (300 MHz, DMSO-d_6) : δ 21.56, 27.70, 67.16, 154.66

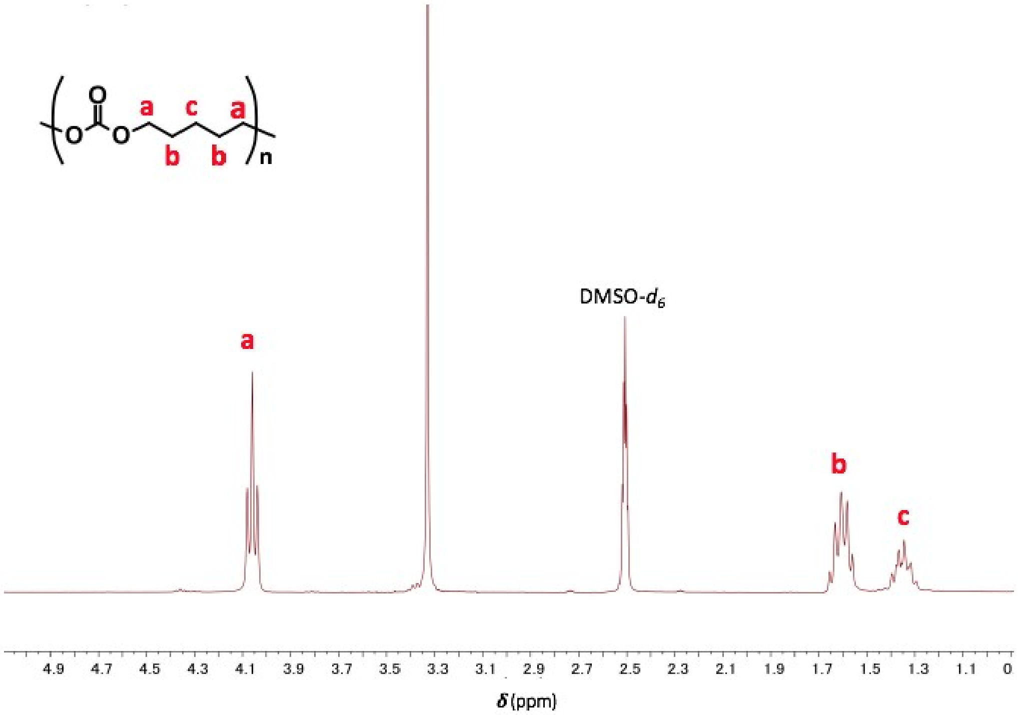

Figure S7. ^{1}H NMR spectrum of **P5C** (DMSO-d_6, 300 MHz).

For the synthesis of **P(3C$_{47}$-5C$_{53}$)**

3C (0.35 g, 1.96 mmol, 0.5 eq.), **5C** (0.50 g, 1.96 mmol, 0.5 eq.), DMC (0.708 g, 7.86 mmol, 2 eq.), DMAP (4.8 mg, 0.039 mmol, 0.01 eq.) were added in a Schlenk flask. The reaction mixture was stirred at 130 °C, 4h, then the temperature was increased at 170 °C under high vacuum condition for overnight. After the reaction, the reaction mixture was dissolved in dichloromethane and precipitated into cold methanol. ^{1}H NMR (300 MHz, DMSO-d_6) : δ 1.34 (m, $OCOOCH_2CH_2C\underline{H_2}CH_2$ (P5C)), 1.60 (m, $OCOOCH_2C\underline{H_2}CH_2C\underline{H_2}CH_2$ (P5C)), 1.94 (m, $OCOOCH_2C\underline{H_2}CH_2$ (P3C)), 4.05 (m, $OCOOC\underline{H_2}CH_2$ (P5C)), 4.14 (m, $OCOOC\underline{H_2}CH_2$ (P3C)), ^{13}C NMR (300 MHz, DMSO-d_6) : δ 21.56, 27.71, 64.24, 67.16, 154.40, 154.53, 154.67

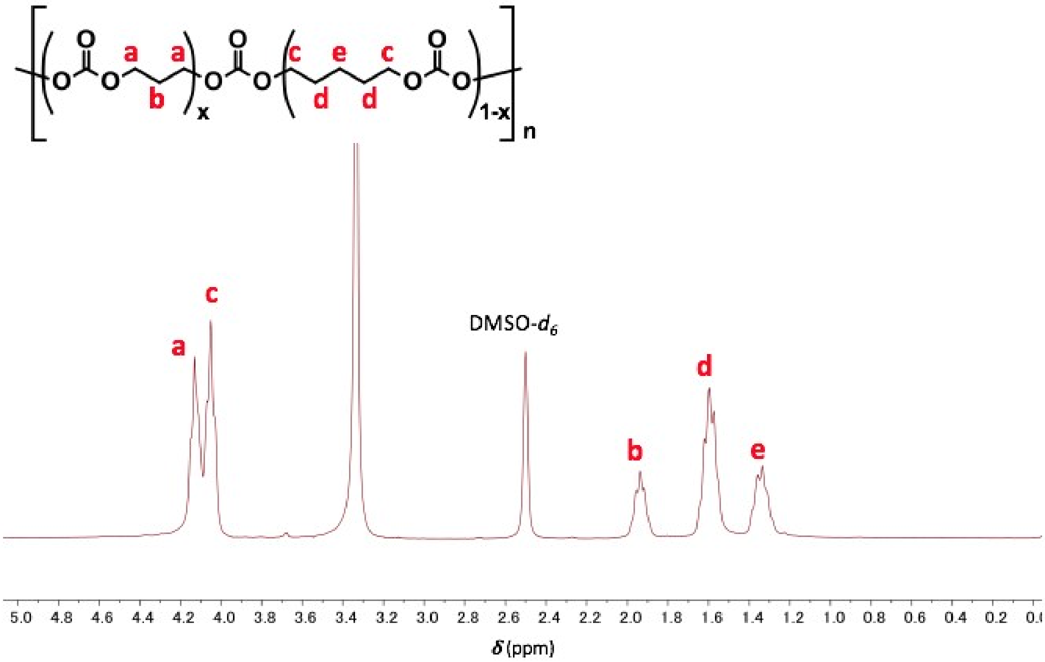

Figure S8. ^{1}H NMR spectrum of **P(3C$_{47}$-5C$_{53}$)** (DMSO-d_6, 300 MHz).

For the synthesis of **P(3C$_{16}$-5C$_{84}$)**

3C (0.175 g, 0.98 mmol, 0.25 eq.), **5C** (0.748 g, 2.94 mmol, 0.75 eq.), DMC (0.708 g, 7.86 mmol, 2 eq.), DMAP (4.8 mg, 0.039 mmol, 0.01 eq.) were added in a Schlenk flask. The reaction mixture was stirred at 130 °C, 4h, then the temperature was increased at 170 °C under high vacuum condition for overnight. After the reaction, the reaction mixture was dissolved in dichloromethane and precipitated into cold methanol. ^{1}H NMR (300 MHz, DMSO-d_6) : δ 1.35 (m, $OCOOCH_2CH_2C\underline{H_2}CH_2$ (P5C)), 1.61 (m, $OCOOCH_2C\underline{H_2}CH_2C\underline{H_2}CH_2$ (P5C)), 1.94 (m, $OCOOCH_2C\underline{H_2}CH_2$ (P3C)), 4.06 (m, $OCOOC\underline{H_2}CH_2$ (P5C)), 4.13 (m, $OCOOC\underline{H_2}CH_2$ (P3C))

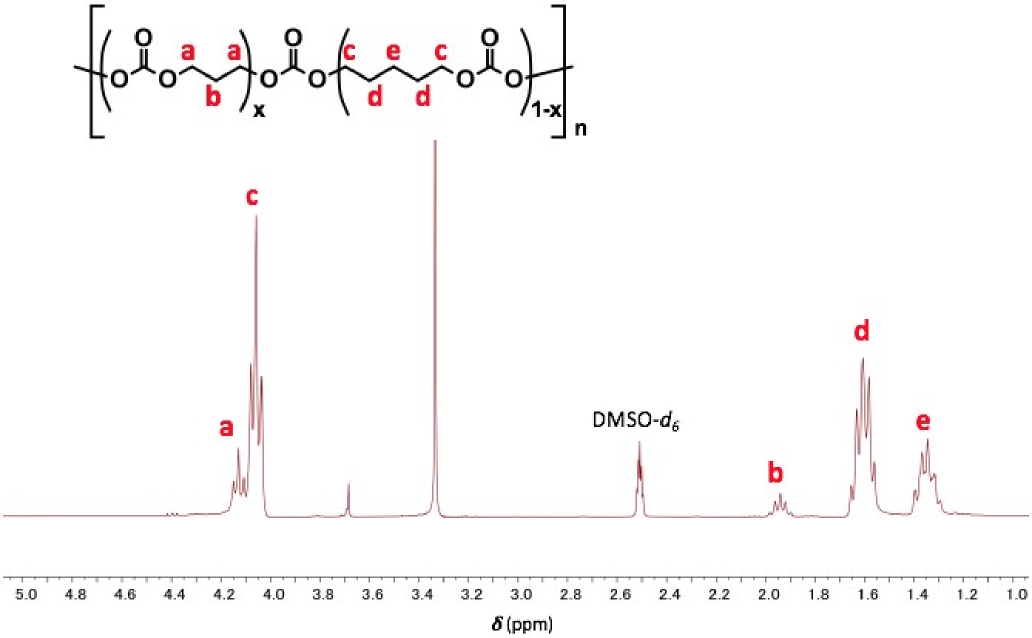

Figure S9. ^{1}H NMR spectrum of **P(3C$_{16}$-5C$_{84}$)** (DMSO-d_6, 300 MHz).

For the synthesis of **P(3C$_{65}$-5C$_{35}$)**

3C (0.525 g, 2.94 mmol, 0.75 eq.), **5C** (0.249 g, 0.98 mmol, 0.25 eq.), DMC (0.708 g, 7.86 mmol, 2 eq.), DMAP (4.8 mg, 0.039 mmol, 0.01 eq.) were added in a Schlenk flask. The reaction mixture was stirred at 130 °C, 4h, then the temperature was increased at 170 °C under high vacuum condition for overnight. After the reaction, the reaction mixture was dissolved in dichloromethane and precipitated into cold methanol. ^{1}H NMR (300 MHz, DMSO-d_6) : δ 1.34 (m, $OCOOCH_2CH_2C\underline{H_2}CH_2$ (P5C)), 1.60 (m, $OCOOCH_2C\underline{H_2}CH_2C\underline{H_2}CH_2$ (P5C)), 1.94 (m, $OCOOCH_2C\underline{H_2}CH_2$ (P3C)), 4.06 (m, $OCOOC\underline{H_2}CH_2$ (P5C)), 4.13 (m, $OCOOC\underline{H_2}CH_2$ (P3C))

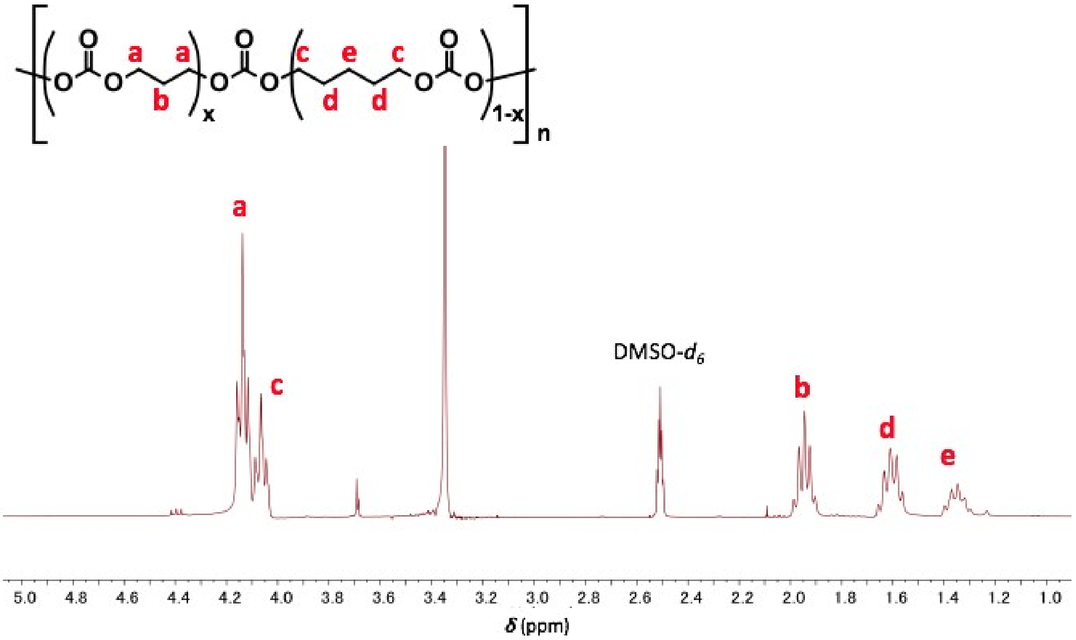

Figure S10. ^{1}H NMR spectrum of **P(3C$_{65}$-5C$_{35}$)** (DMSO-d_6, 300 MHz).

5. ^{13}C NMR spectra of aliphatic polycarbonates

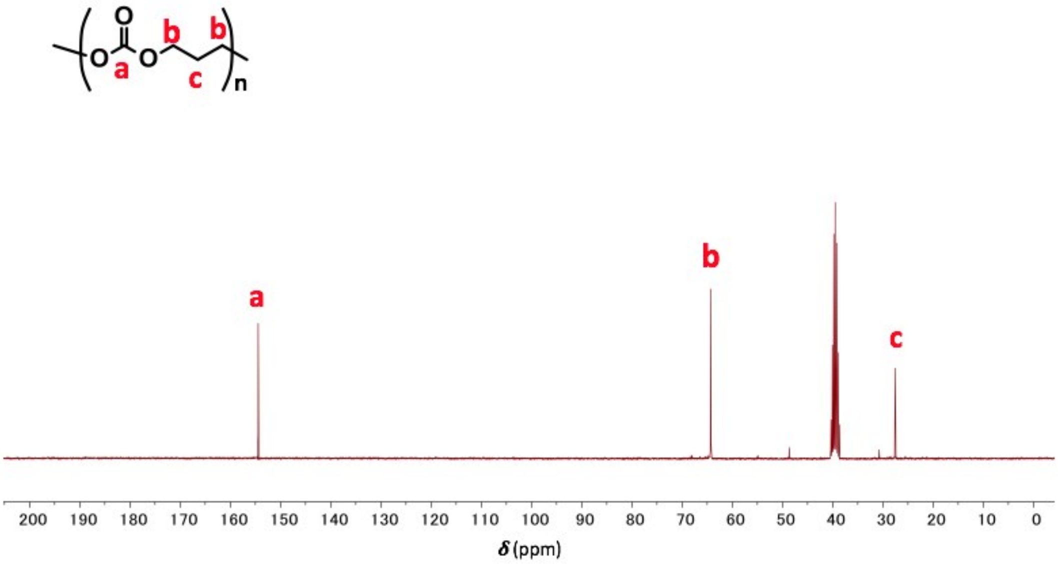

Figure S11. ^{13}C NMR spectrum of **P3C** (DMSO-d_6, 300 MHz).

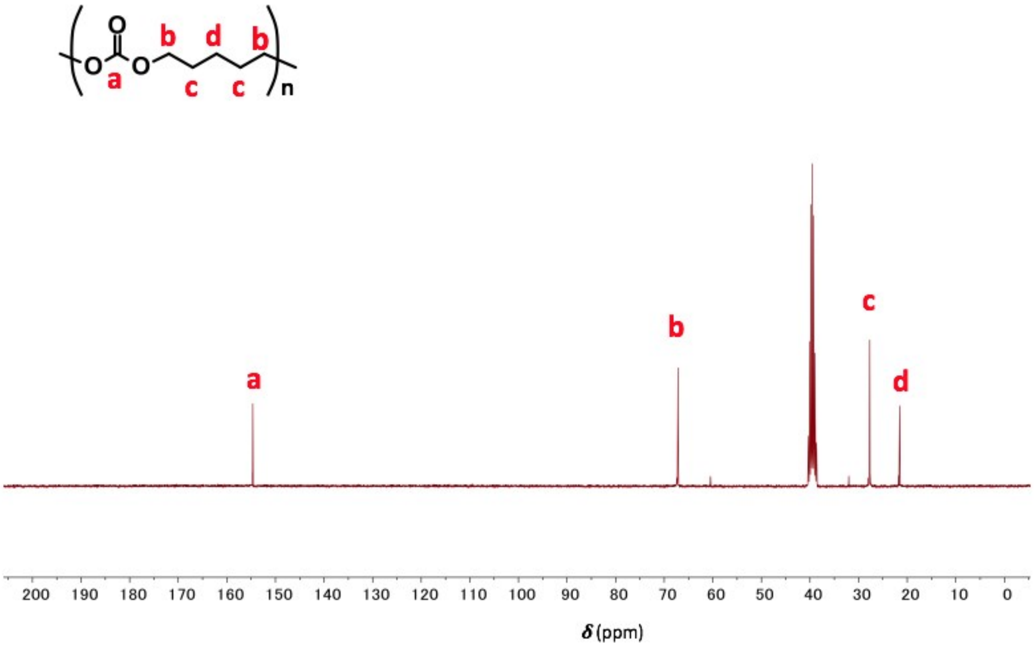

Figure S12. ^{13}C NMR spectrum of **P5C** (DMSO-d_6, 300 MHz).

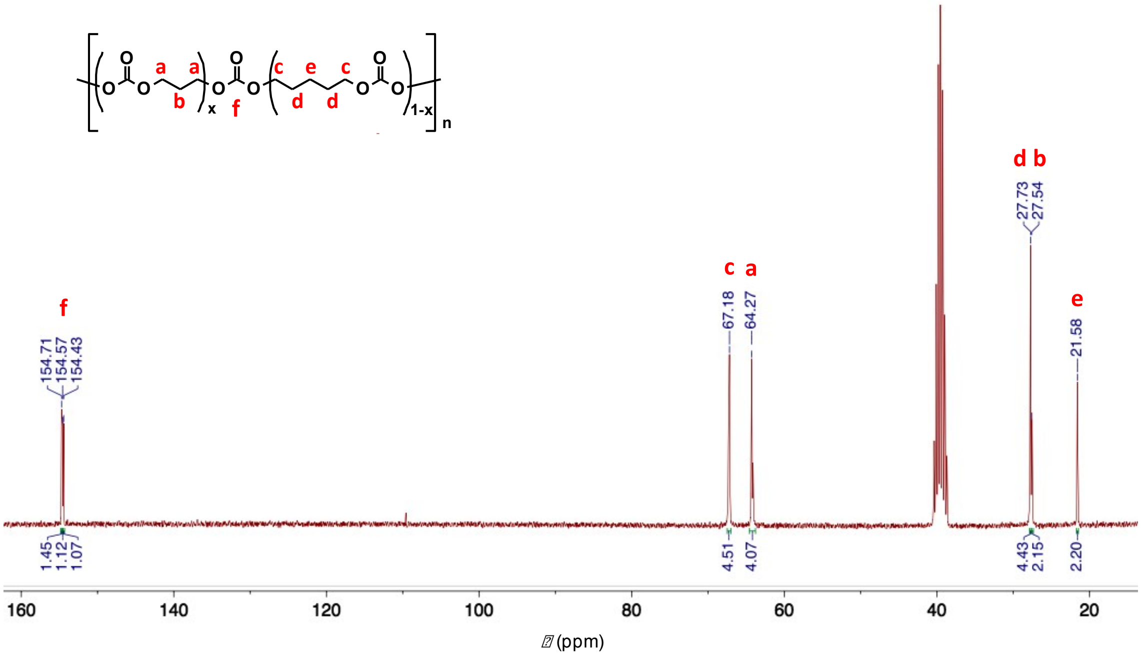

Figure S13. ^{13}C NMR spectrum of **P(3C$_{47}$-5C$_{53}$)** (DMSO-*d*$_6$, 300 MHz).

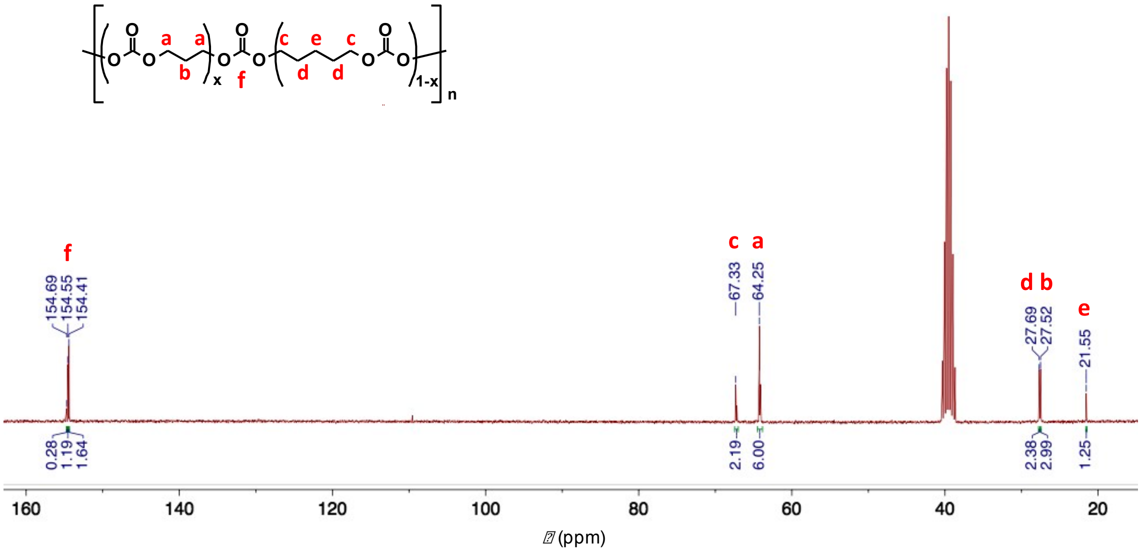

Figure S14. ^{13}C NMR spectrum of **P(3C65-5C$_{35}$)** (DMSO-*d*$_6$, 300 MHz).

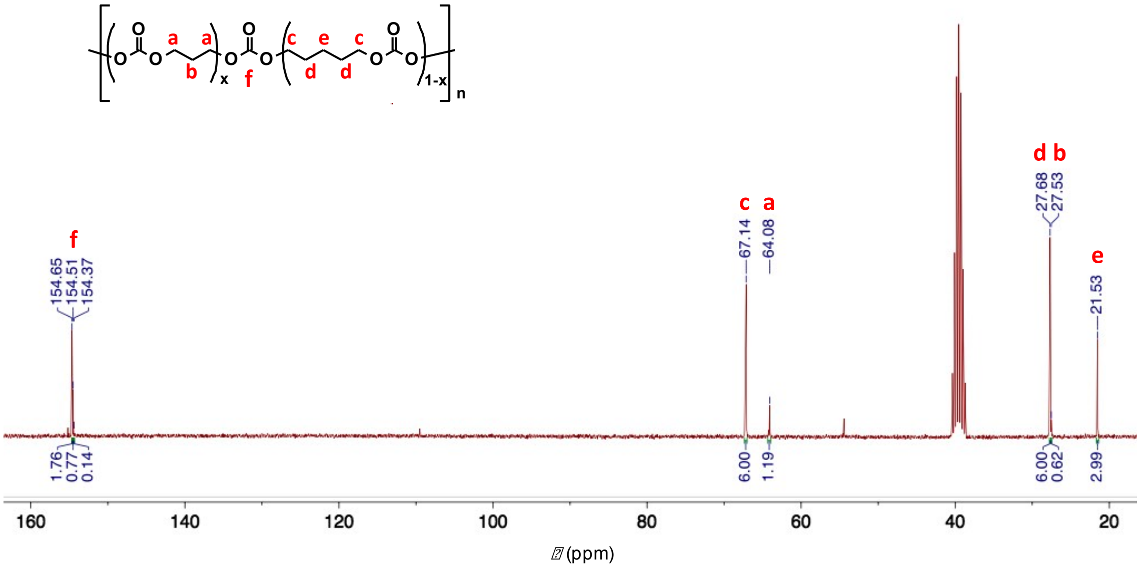

Figure S15. ^{13}C NMR spectrum of **P(3C$_{16}$-5C$_{84}$)** (DMSO-d_6, 300 MHz).

6. Thermogravimetric Analysis

The thermal stability was analysed by a TGAQ500 (TA instrument) under nitrogen atmosphere. Samples of 5–10 mg were disposed in a Palladium pan for being heated from 40 to 600 °C at a rate of 10 °C min^{-1}.

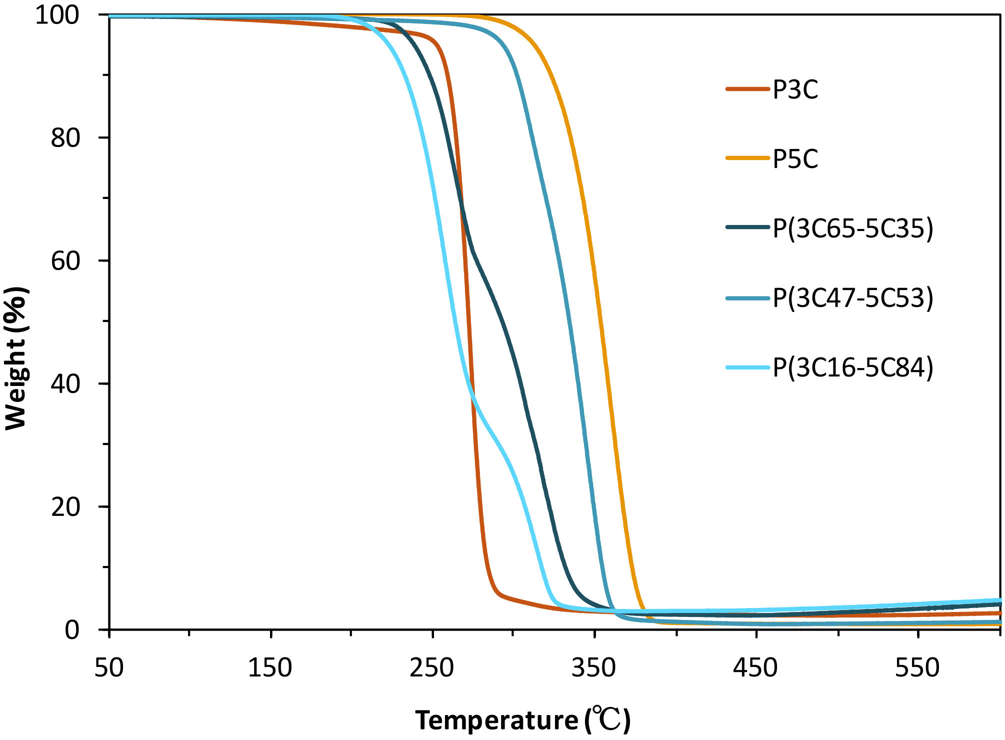

Figure S16. Thermogravimetric analysis for the five polymers synthesised in this publication

7. Electrochemical experiments

Lithium transference number (LTN), AC impedance spectroscopy, and electrochemical stability were characterized in a VMP3 (Biologic, Claix, France) potentiostat and symmetric cell test in Neware. The cells were assembled in an argon-filled glove box (MBraun <0.5 ppm O_2, <0.5 ppm H_2O) in CR2032 type coin cell. The electrolytes were sandwiched between two lithium disks for LTN and symmetric cell analyses, and between lithium disks and stainless steel for electrochemical stability evaluation. The polymer electrolyte surface area for lithium transference number and electrochemical stability was 0.07 cm^2, whereas for the symmetric cell analysis the surface area was 0.5 cm^2. Before the experiments, the cells were left stabilizing for 6 h at 70 °C. Lithium transference number was calculated based on Bruce and Vincent method at 70 °C.[1] Impedance analysis was determined by AC impedance spectroscopy over the frequency range from 100 mHz to 1 MHz with an amplitude of 10 mV. The symmetric cell tests were completed applying 0.05 mA cm^{-2} during 30 min. Electrochemical stability window was calculated by linear sweep voltammetry (LSV). The anodic limit was evaluated between open circuit potential (OCV) and 6 V vs. Li^+/Li at a constant rate of 1 mV s^{-1}.

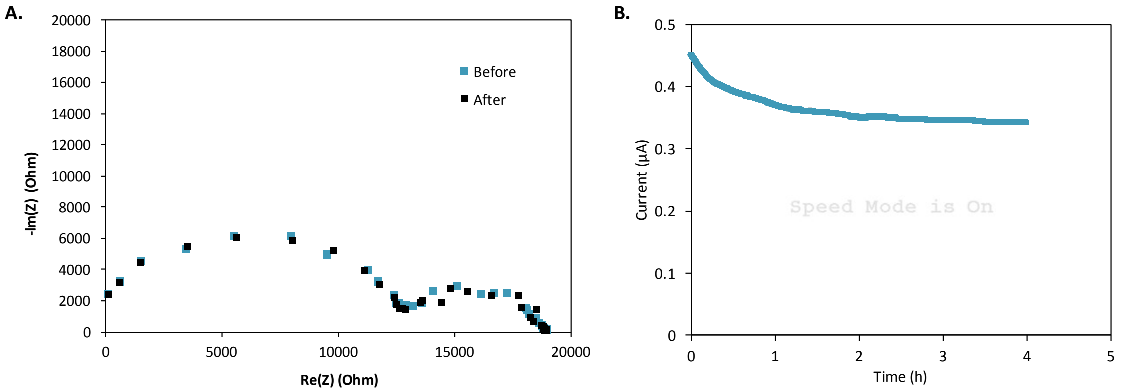

Figure S17. Lithium transference measurement analysis at 70 ºC. **A.** PEIS after and before the chronoamperometry and **B.** chronoamperometry applying 10 mV.

Table S1. Data used for in the equation for the calculation of LTN based on Bruce

I_i (μA)	I_s (μA)	$R_{b,i}$ (Ω)	$R_{b,s}$ (Ω)	$R_{lithium,i}$ (Ω)	$R_{lithium,s}$ (Ω)	ΔV (mV)	LTN
0.772	0.341	13128	5789	12961	5921	10	0.45

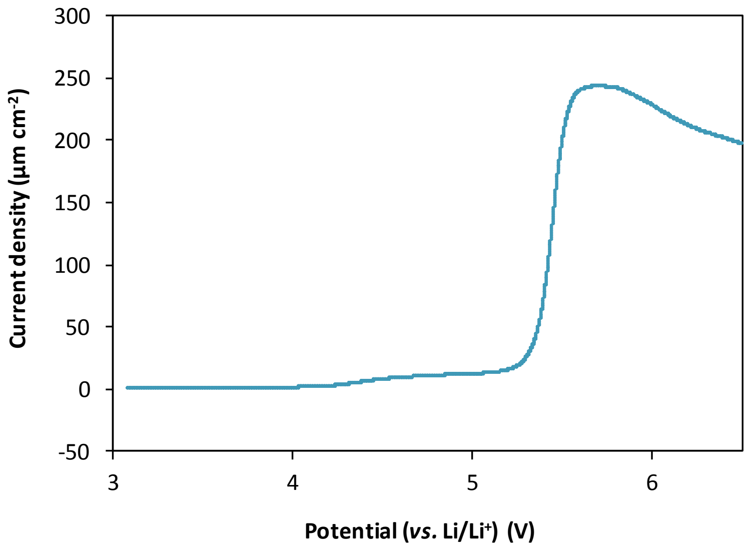

Figure S18. Lineal sweep voltammetry at 70 ºC, 1mV s^{-1} scan rate

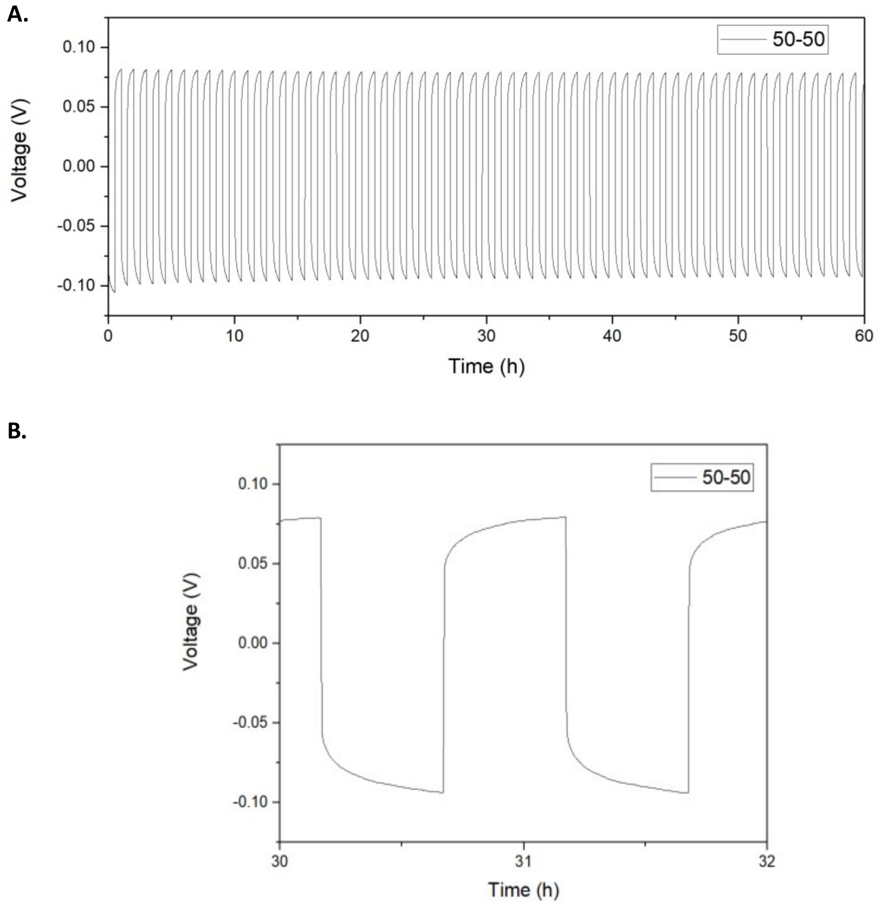

Figure S19. A. Symmetric cell test at 70 ºC applying 0.05 mA cm^{-2} and **B.** Symmetric cell analysis profiles, zoom between 30 and 32 h,

8. References

1 J. Evans, C. A. Vincent and P. G. Bruce, *Polymer*, 1987, **28**, 2324–2328.