

## Supporting Information

# A Mechanically Robust Yet Highly Conductive Diblock Copolymer Solid Polymer Electrolyte for Ambient Temperature Battery Applications

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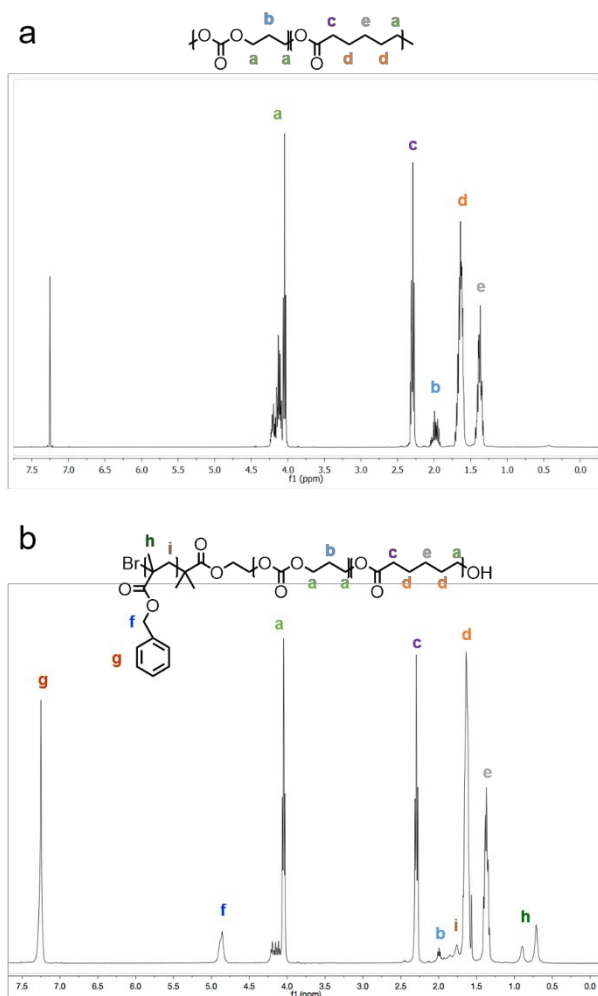
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### Present Addresses

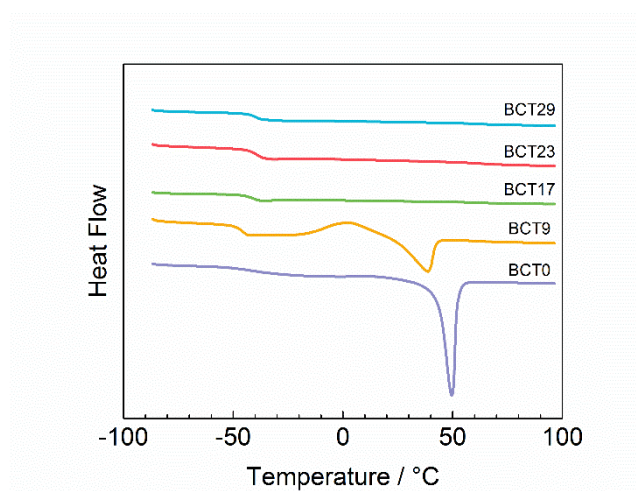
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### Author Contributions

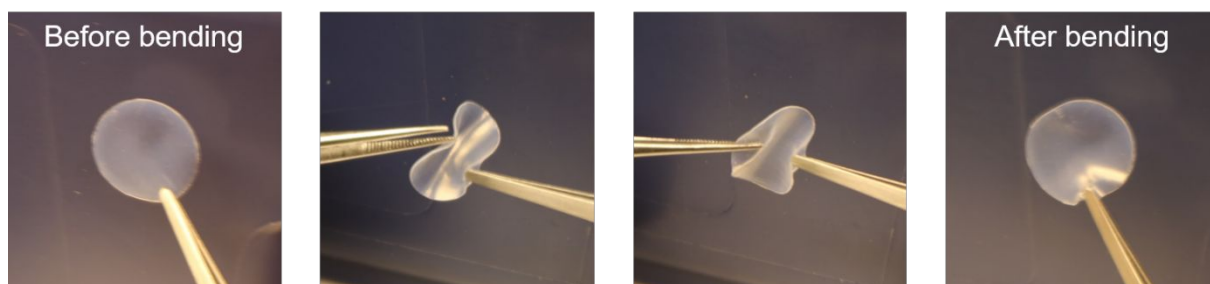
<sup>‡</sup> These authors contributed equally.



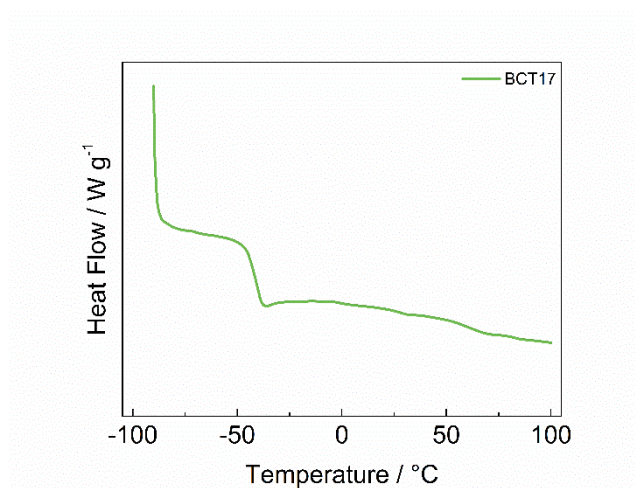
**Figure S1.**  $^1\text{H}$  NMR spectra of (a) PCL-PTMC and (b) BCT polymer.



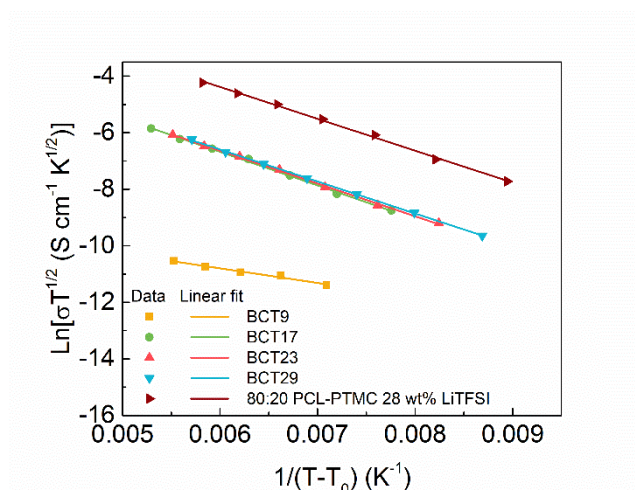
**Figure S2.** DSC traces for the pure BCT and the BCT-based polymer electrolytes containing different salt concentrations.



**Figure S3.** Images of a self-standing and easy to handle BCT17 polymer electrolyte film.



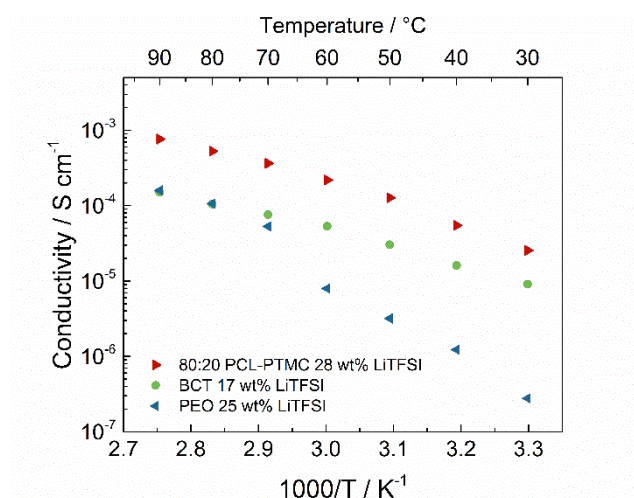
**Figure S4.** DSC trace for the BCT17 electrolyte. No clear phase separation can be seen, as indicated by the single clear  $T_g$  at ca.  $-40\text{ }^{\circ}\text{C}$ .



**Figure S5.** Ionic conductivity fitting with the Vogel–Fulcher–Tammann (VFT) equation to determine the slope and calculate the activation energy for different solid polymer electrolytes. Fitting of BCT9 electrolyte was only done with the values above the deflection point (above  $50\text{ }^{\circ}\text{C}$ ).

**Table S1.** Activation energies of the polymer electrolytes calculated with the Vogel–Fulcher–Tammann (VFT) equation. The values were obtained from the slope of  $\ln \sigma$  vs  $1/(T-T_0)$  and multiplied by the universal gas constant,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Polymer electrolyte	Slope (K)	$E_a$ (kJ mol <sup>-1</sup> )
BCT9	516.5	4.3
BCT17	1187.7	9.9
BCT23	1159.1	9.6
BCT29	1131.95	9.4
80:20 PCL-PTMC 28 wt% LiTFSI	1127.8	9.4



**Figure S6.** Comparison of the ionic conductivities for electrolytes BCT17 (green circles), 80:20 PCL–PTMC (red right-pointing triangles), and PEO (blue left-pointing triangles).

**Table S2.** The obtained values and confidence limits which were inserted into the Bruce-Vincent equation to calculate the apparent transference number.

Parameter	Value	95% confidence limit
Initial current ( $I^0$ )	16.5 $\mu\text{A}$	2 %
Current at steady-state ( $I^s$ )	10.9 $\mu\text{A}$	5 %
Applied potentiostatic bias ( $\Delta V$ )	20 mV	2 %
Initial polymer electrolyte interface resistance ( $R^0$ )	141 $\Omega$	5 %
Polymer electrolyte interface resistance at steady-state ( $R^s$ )	155 $\Omega$	5 %
Apparent transference number ( $T_+$ )	0.64 $\pm$ 0.04	

The confidence limits reported in the table were estimated based on instrumental accuracy, quality of data, and fit from electrochemical impedance spectroscopy. The confidence limit for the apparent transference number value was calculated using a Monte Carlo method, in which normal distributions of all the input values with specified 95 % confidence limits and which are then used to calculate a resulting distribution of  $T_+$  values. This calculation was implemented using the following code in R.

```

# rnorm_cl generates a normal distribution with 'n' data points, a specified mean
and a standard
# deviation calculated from a 95% confidence limit 'cl'.
rnorm_cl <- function(mean, n, cl) { rnorm(n, mean = mean, sd = (cl * mean/100) /
1.96) }

# How to use this function:
# I0 and Iss are currents with units of A.
# R0 and Rss are resistances with units of Ohms.
# Values beginning with 'e' are confidence limits in percent, which need to be
determined as appropriate
# for the specific measurement.
# The function will return a value for F+/apparent T+ with 95% confidence limits.
Fplus_cl <- function(I0, Iss, R0, Rss, DV = 0.01, eR0 = 5, eRss = 5, eDV = 2, eI0 =
2, eIss = 5) {
  I0 <- rnorm_cl(I0, 10000, eI0)
  Iss <- rnorm_cl(Iss, 10000, eIss)

  DV <- rnorm_cl(DV, 10000, eDV)

  R0 <- rnorm_cl(R0, 10000, eR0)
  Rss <- rnorm_cl(Rss, 10000, eRss)

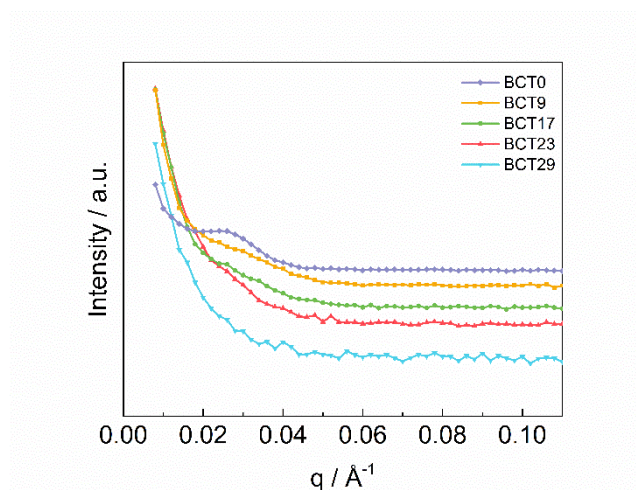
  a <- data.frame(I0 = I0, Iss = Iss, DV = DV, R0 = R0, Rss = Rss)

  b <- a %>%
    mutate(Fplus = (Iss/I0) * ((DV - (I0*R0))/(DV - (Iss*Rss))))

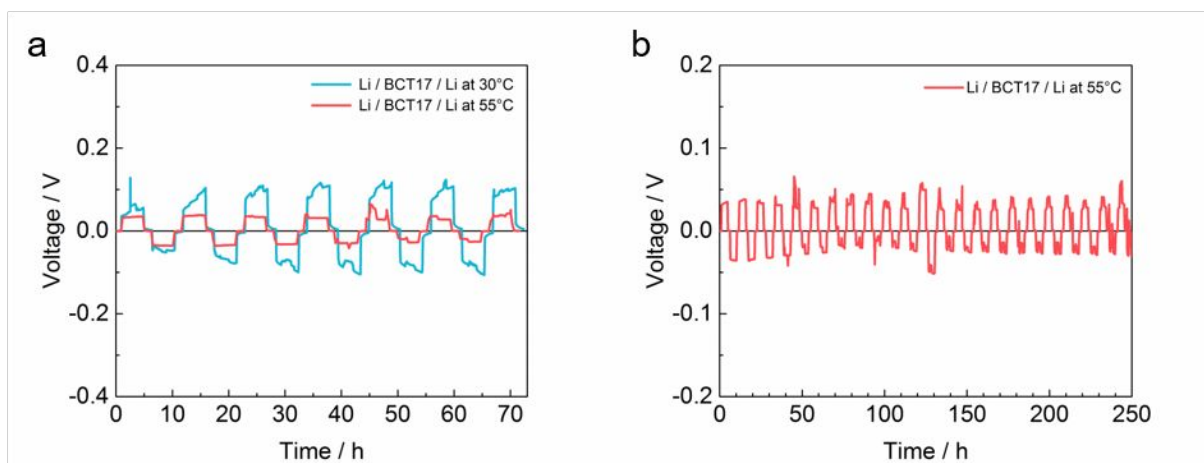
  return(c(mean = mean(b$Fplus), cl = sd(b$Fplus) * 1.96))
}

Fplus_cl(I0 = 16.5E-6, Iss = 10.9E-6, DV = 0.02, R0 = 141, Rss = 155)

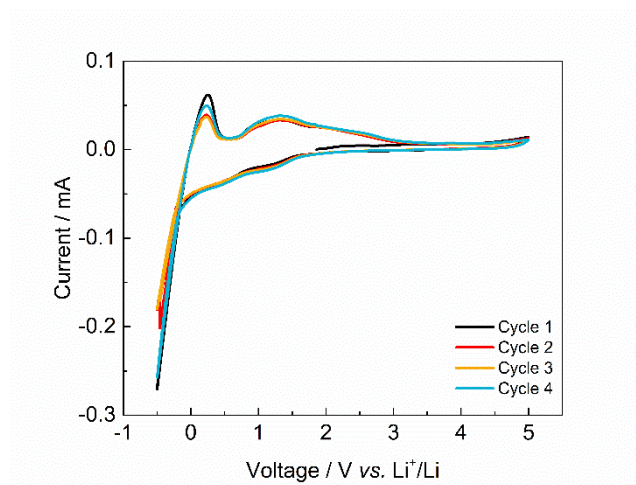
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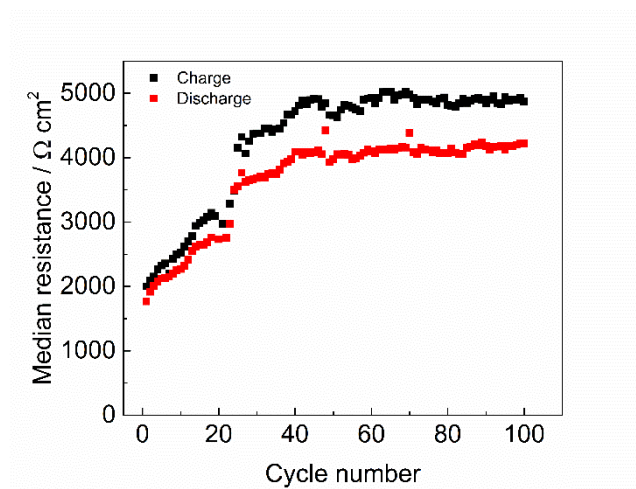
**Figure S7.** SANS curves for the BCT series at 25 °C. The curves are shifted vertically for clarity. The scattering peak intensity decreases with LiTFSI loading, indicating that there is no clear phase separation in these polymer electrolytes. Nevertheless, this could also be due to poor scattering contrast from both blocks.



**Figure S8.** Symmetric Li | BCT17 | Li cells polarized for 4 h at  $0.013 \text{ mA cm}^{-2}$  current density with 90 min rest between plating and stripping cycles. (a) At 30 °C (blue line) and 55 °C (red line), and (b) long term cycling at 55 °C.



**Figure S9.** Cyclic voltammetry results for electrolyte BCT17 with a scan rate of  $1 \text{ mV s}^{-1}$  with stainless steel as the working electrode and metallic lithium as a combined reference and counter electrode.



**Figure S10.** Intermittent current interruption experiment on a half-cell design of Li|BCT17|LiFePO<sub>4</sub>. The graph shows the median cell resistance as a function of cycling number, with the resistance reaching a plateau at about 50 cycles. A plausible explanation is that a delayed SEI layer is formed during this time.