## **Electronic Supplementary Information**

## Structural origins of the capacity fading in the lithiumpolyimide battery

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Fig. S2. Coulombic efficiencies (a, c, e) and evolution of the charge-discharge characteristics (b, d, f) of the batteries cycled at different current rates: 2C (a-b); 0.5C (c-d) and 0.1C (e-f). Cycle numbers are indicated near the corresponding curves.

Fig. S3. Coulombic efficiencies (a) and evolution of the charge-discharge characteristics (b) of batteries assembled with polymer electrolyte (current rate is 0.5C). Cycle numbers are indicated near the corresponding curves.

Fig. S4 FTIR spectrum of the NDI-HY

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Table S1. Chemical analysis of the NDI-HY polyimide



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b



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Fig. S5. ESI-MS mass spectra of the electrolyte extracted from the reference non-cycled battery (a) and the battery cycled for 200 cycles at 0.1C (b). Molecular structure of the representative NDI-HY fragment responsible for the appearance of ions  $M^{2+}$  (m/z=272), [M+EC]<sup>2+</sup> (m/z=316), [M+2EC]<sup>2+</sup> (m/z=360), [M+3EC]<sup>2+</sup> (m/z=404) and [M+4EC]<sup>2+</sup> (m/z=448), where EC is ethylene carbonate.



Fig. S6. UV-vis absorption spectra of the electrolyte extracted from the reference non-cycled battery, the battery cycled for 200 cycles at 0.1C and pure naphthalene diimide C6-NDI (a). Molecular structure of C6-NDI (b). Vertical lines in (a) marking characteristic NDI absorption features are given as a guide for eye.

Table S1. Chemical ana	lysis of the NDI-HY	polyimide
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	C, %	H, %	N,%
Calculated	63.65	1.53	10.60
Found	63.37	1.61	10.42

а