Supporting Information

Perylene Polyimide Based Organic Electrode Materials for Rechargeable Lithium Batteries

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Synthesis and characterization of perylene diimide polymers HP, EDP and UP: A mixture of 2 mmol of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 2 mmol of diamine, 5.0 g of imidazole and 2 mmol of zinc acetate was heated with stirring at 140 °C for 5 h. The mixture was cooled to room temperature, poured into 1 N hydrochloric acid and stirred for 15 min. Precipitate was collected through vacuum filtration and washed with boiling saturated potassium carbonate solution followed by distilled water for three times and dried in air at 100 °C. Obtained dried material was then washed several times with DMSO until the washings became colorless to remove the short oligomers from the mixture. Final product is highly insoluble in organic solvents.

1. *Hydrazine–perylene diimide polymer (HP):* Hydrazine hydrate was used as diamine to synthesise the HP. Red brown needle like solid was obtained with a yield of 89%. Decomposition temperature 645 °C; Solid state ¹³C MAS NMR (100 MHz, δ): 171.97 (C=O), 154.79 (Ar-C), 132.61 (Ar-C), 119.82 (Ar-C). IR (KBr): v = 1700 (s), 1663 (s), 1592 (s), 1400 (s), 1367 (s), 1255 (s) cm⁻¹; Anal. calcd. for (C₂₄H₈N₂O₄)_n: C 73.85, H 2.58, N 7.18%; found: C 73.68, H 2.85, N 7.14%.

2. Ethylenediamine-perylene diimide polymer (EDP): Ethylenediamine was used as diamine to synthesise the polymer EDP. Black coloured solid was obtained as the product with a yield of 83%. Decomposition temperature 620 °C ; Solid state ¹³C MAS NMR (100 MHz, δ): 160.34 (C=O), 144.61 (Ar-C), 136.4 (Ar-C), 53.24 (CH₂). IR (KBr): $\nu = 1705$ (s), 1660 (s), 1592 (s), 1495 (s), 1400(s), 1356(s), 1250 cm⁻¹ (s) ; Anal. calcd. for (C₂₆H₁₂N₂O₄)_n: C 74.64, H 3.37, N 6.70%; found: C 74.57, H 3.81, N 7.06%.

3. Urea-perylene diimide polymer (UP): Urea (Carbonyl diamine) was used as diamine to synthesise the polymer UP. Dark red coloured powder was obtained with a yield of 74%. Decomposition temperature 625 °C ; Solid state ¹³C MAS NMR (100 MHz, δ): 173 (C=O),

146.53 (Ar-C), 133.4 (Ar-C), 115.99 (Ar-C). IR (KBr): v = 1760 (s),1715(s), 1682 (s), 1587 (s), 1435 (s), 1405 (s), 1360(s), 1320 (s), 1265 cm⁻¹ (s); Anal. calcd. for $(C_{25}H_8N_2O_5)_n$: C 71.77, H 2.41, N 6.70%; found: C 71.10, H 2.59, N 6.48%.

Electrochemical testing: For electrochemical measurements, coin-type cells (CR2032, *Hohsen Co. Ltd, Japan*) consisting of a working electrode and a lithium foil counter electrode separated by a Whatman glass fibre filter were used. The working electrodes were prepared by mixing the active material with 30 wt% acetylene black and 10 wt% polyvinylidene difluoride (PVDF) binder. It is then made in the form of slurry by adding one or two drops of N-methyl pyrrolidone (NMP) and pasted onto a stainless steel current collector. 1 M solution of LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC= 1:1 v/v) was used (*Solvionic, France*) as the electrolyte. The cells were assembled in an argon-filled glove-box (*MBraun Unilab, Germany*). Both the galvanostatic charge/discharge and cyclic voltammetry experiments were performed in the potential range of 1.5–3.5 V vs. Li⁺/Li using a Biologic SAS VMP3 electrochemical work station, at different current densities and scan rates. EIS measurments were carried out between a frequency range of 10 mHz to 40 kHz with a sinusoidal signal of 10 mV amplitude.



Figure S1. Thermogravimetric analysis curves of **EDP**, **HP**, **UP** and **PTCDA**. Measurements were carried out under nitrogen atmosphere at a ramp rate of 10°C min⁻¹.



Figure S2. A representative scheme indicating of mechanism of lithiation and delithiation happening duriing the charge- discharge process of HP based- rechargeable lithium battery. A similar mechanistic model involving a two electron reaction is equally applicable for all the proposed polymides.



Figure S3. Cycling performance of a) HP; b) UP; c) EDP at different current densitites, galvanostatically cycled between 1.5 and 3.5 V *vs.* Li⁺/Li and d) rate capability study of polymers HP, UP and EDP, showing the discharge capacities at different current rates.



Figure S4. FT-IR spectra of pristine UP (blue) and lithiated UP (UP-Li) (red).

Name	Theoretical Specific capacity (mAhg ⁻¹)	Observed Specific capacity (mAhg ⁻¹)	Average cell potential (V)	Maximum Energy density (Whkg ⁻¹)	Maximum Power Density (Wkg ⁻¹)
PTCDA	147.2	54.6	1.73	94.5	86.3
EDP	106.2	85.8	2.24	192.2	46.5
HP	116.5	110.2	2.35	259	958
UP	196.7	130	2.43	315.9	934

Table S1. Table showing the electrochemical parametres of parent PTCDA and the derivatives polymers. Theoretical specific capacity is calculted based on a more realistic two electron redox process as shown in Figure S2 except for UP. Theoretical specific capacity of UP is calculted based on a reversible three electrone redox process. Observed (stable) capacity shown in the table are obtained by galvanostatic -charge discharge at a current rate of 50 mAg⁻¹. Average discharge potential was measured at the half discharge capacity.