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Perylene-polyimide-Based Organic Electrode Materials for Rechargeable Lithium Batteries

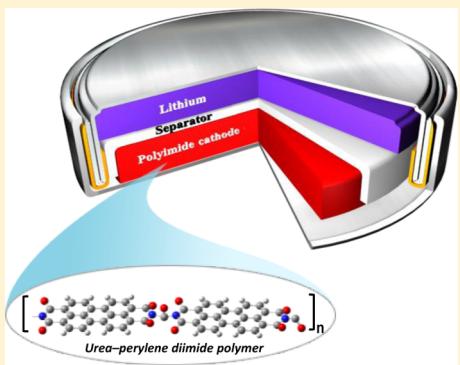
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Supporting Information

ABSTRACT: Organic materials for Li-ion battery application continue gaining attention due to the virtue of low cost, environmental benignity, and so on. A new class of electroactive organic material called polyimides is particularly important due to the extra stability exhibited at higher current rates. High-performance rechargeable lithium battery cathodes based on polyimides of 3,4,9,10-perylenetetracarboxylic acid-dianhydride are prepared. The novel electrodes exhibit good rate capability and improved cycling stability, which result from their combined beneficial properties such as the presence of additional carbonyl groups, favorable band gap, and enhanced conductivity, making it a potential material for greener and sustainable electrochemical storage devices.



SECTION: Energy Conversion and Storage; Energy and Charge Transport

Storage and utilization of sustainable energy via an environmentally friendly route is an important aspect of energy economy.^{1–3} With a growing need for clean and efficient energy-storage technologies, rechargeable Li-ion batteries are undoubtedly the state-of-the-art and hence continue to gain both scientific and commercial importance for their applications in portable electronics and vehicular sector.^{4–6} However, designing advanced batteries that are highly energy efficient and eco-friendly is still a major challenge. The current Li-ion battery technology with active inorganic insertion electrode materials such as LiCoO₂ fails to fulfill the demand in terms of safety and sustainability. Recently, there has been wide interest toward developing “greener and sustainable” rechargeable lithium batteries based on organic electrode-active materials.^{7–10} Research on organic electrodes for rechargeable lithium batteries, although started several years back, did not gain much importance until recently, partially due to their poor performances and wide acceptance of transitional-metal-based inorganic electrodes. Transition from inorganic to organic material-based electrodes could be a possible alternative, and several groups have turned toward “organic approach”, thanks to the rich and versatile chemistry available for organic synthesis that allows the design of electrode materials with high level of control over the functionalities and tunable redox properties without the use of heavy metals and high-temperature synthesis.¹ In recent years, several redox-active organic materials such as organosulphur,¹¹ radical poly-

mers,^{12,13} and carbonyl¹⁴-based compounds have been studied as electrodes for Li-based batteries and were reported to exhibit reversible reactivity with Li. However, the performance characteristics of such organic electrodes for their application in Li-ion battery were limited due to several factors such as electrode dissolution, thermal instability, and so on. Reversible redox properties of carbonyl-based organic molecules have been extensively studied by several groups.^{1,10,14–16} Nevertheless, organic-based materials present some drawbacks such as low thermal stability, low conductivity, and solubility in organic electrolytes compared with existing inorganic-based electrode materials.¹ Efforts have been undertaken to design new materials with improved functionalities resulting in stable reversible redox activities. However, it is extremely challenging to design organic-based electrodes with high redox potential versus Li. Recently, a lithiated 1,4,5,8-naphthalenetetraol formaldehyde polymer has shown reversible cycling up to 4.2 V versus Li, however, with a poor capacity and low cyclic stability.¹⁷ The mechanism of lithiation/delithiation in organic compounds involves reversible redox reaction of the respective organic functional groups such as keto, carboxylate, anhydride, and so on along with insertion/removal of Li⁺ ions at the respective redox centers.^{14,16,18–22} Diverse synthetic strategies

Received: August 14, 2013

Accepted: September 9, 2013

Published: September 9, 2013

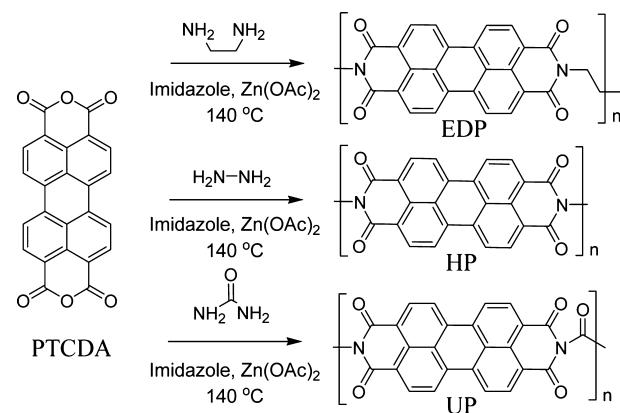


have been undertaken to improve the performance of the organic electrodes, for example, by chemical substitution²³ or polymerization.^{1,24–26} Semiconducting organic π -conjugated polymers containing aromatic core or unsaturated bonds, which are essential for the conduction of electrons, are a key requirement for electrode material. Polymerization also prevents electrode dissolution in nonaqueous electrolyte, leading to good cyclic stability.¹ Han et al. reported the performance of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) sulfide polymer as the positive electrode with stable capacity retention of 130 mAhg⁻¹.²⁰ Attempts were made to utilize the inherent high theoretical capacity of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)²¹ compared with PTCDA.²⁰ Polyimides based on benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA) and NTCDA, PTCDA have been studied for their electrochemical performance versus Li.^{27–29} Lithium enolates formed in such systems are stabilized by the conjugation extended by core π electrons and complement the cycling stability and reversibility.²⁹ By virtue of the flexibility in molecular design and diverse functionalities available, it is interesting to explore new organic-based electrode materials having carbonyl functionalities which will effectively improve the battery performance. Here we report the design and fabrication of PTCDA polyimide-based organic electrodes. Detailed studies of the electrochemical behavior of polyimides of PTCDA synthesized using ethylenediamine, hydrazine, and urea as cathodes for rechargeable lithium battery applications are reported. We show that these novel polymeric carbonyl derivatives can be reversibly cycled at high current rates. Our approach to use the additional carbonyl group from urea polymerization resulted in improved lithium storage and better cyclic stability.

PTCDA has a stable aromatic core with two anhydride groups, which offer a high theoretical capacity of 273 mAhg⁻¹ and high reduction potential with respect to Li.²⁰ Some of the performance issues of PTCDA such as low cyclic stability, material solubility, and degradation can be addressed by polymerizing it with a suitable reagent that in turn provides a channel for the π -electron delocalization of the perylene core. PTCDA can be polymerized through (i) bay or (ii) imide region, making it possible to possess different electronic and redox properties. Polymerization of PTCDA through the imide region using diamines can result in significant increase in the conductivity and kinetics of electron transfer. A generalized approach for polymerization of molecules containing two anhydride functionalities on either end was developed by Song et al. through the use of diamines.²⁹ Imide functional groups formed as a result of polyimidization using diamines leaves carbonyl groups ($C=O$) intact, which are necessary for reversible Li⁺ insertion/deinsertion.

Polyimide derivatives of PTCDA were synthesized through imidization of PTCDA using hydrazine, ethylenediamine, and carbonyl diamine (urea) generating HP, EDP,²⁸ and UP polymers, respectively (Scheme 1) and characterized using various spectroscopic and analytical techniques viz. FT-IR spectroscopy, CP-MAS NMR spectroscopy, CHN elemental analysis, scanning electron microscopy, powder X-ray diffraction, thermogravimetric analysis, and so on. Perylene polyimides thus obtained show poor solubility in common organic solvents. PTCDA shows two broad infrared vibrational bands at 1774 and 1720 cm⁻¹, whereas HP exhibits sharp bands centered around 1700 and 1663 cm⁻¹, which are associated with C=O asymmetric and symmetric stretching frequencies,

Scheme 1. Synthetic Scheme for the Polymers EDP, HP, and UP



respectively (Figure 1a). Similar shifts in IR frequencies are obtained for EDP and UP. Observed significant red shift in the

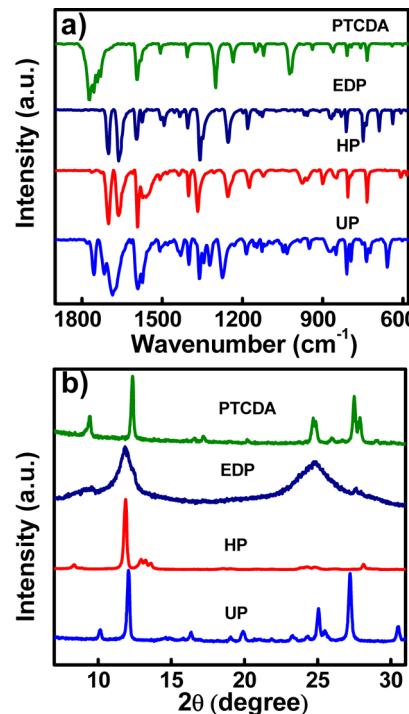


Figure 1. (a) FT-IR spectra and (b) powder X-ray diffraction patterns for PTCDA, EDP, HP, and UP.

carbonyl stretching frequency (~ 1700 and 1663 cm⁻¹) and the absence of peak at 1774 cm⁻¹ in HP, EDP, and UP when compared with PTCDA confirms the conversion of anhydride to imide functionality.³⁰ UP exhibited an additional vibrational band centered around 1755 cm⁻¹ that could be attributed to the IR absorption of carbonyl group in the urea moiety. Powder X-ray diffraction patterns of PTCDA and the polymers show well-crystalline nature, except for EDP (Figure 1b). A systematic shift in the carbon peaks corresponding to perylene diimide core in the solid-state ^{13}C MAS NMR spectra of HP, EDP, and UP when compared with the model derivative PTCDA confirms the formation of imide in polymers (see Supporting Information: Synthesis and Characterization). In addition, the presence of aliphatic carbon in the solid-state ^{13}C

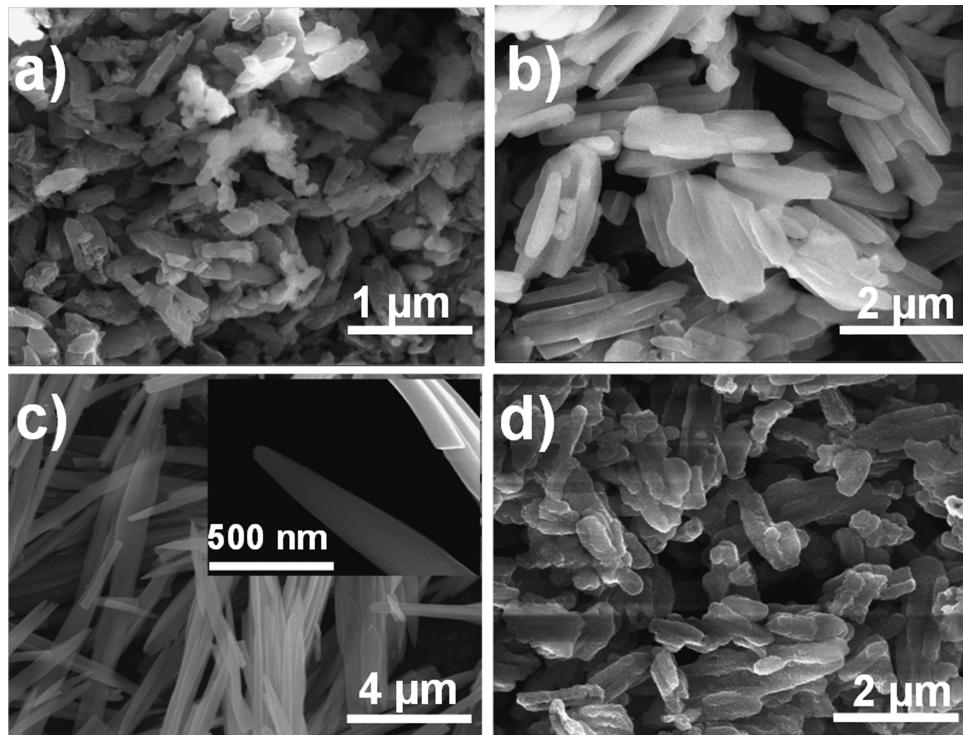


Figure 2. SEM micrographs of PTCDA and polyimide derivatives. Flake-like morphologies are obtained in the SEM images for PTCDA (a), EDP (b), and UP (d), while HP shows needle-like morphology (c). The inset shows high-resolution SEM image of HP.

MAS NMR spectra confirms the presence of ethylene unit in EDP.

SEM images reveal flake-like morphology for EDP and UP similar to the parent PTCDA, as shown in Figure 2a,b,d. In contrast, SEM image of HP shows narrow needle-like morphology (Figure 2c). The peculiar needle-like morphology of HP could be due to the structural rigidity imparted by shortest linker employed called hydrazine. Polymerization of PTCDA through the imide region provides a stable backbone with high thermal stability, as evident from thermogravimetric analysis curves (Figure S1, Supporting Information).

Electrochemical performances of the three polymers (HP, EDP, and UP) and the parent PTCDA have been studied versus Li in coin-type battery test cells using lithium metal foil as negative electrode and by employing cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) measurements. (See the Supporting Information for more details of electrode preparation and characterization procedures.) Initially the cells were discharged to 1.5 V, followed by charging to 3.5 V, at the same constant current density. Despite minor structural variation upon polymerization, the polymers EDP, HP, and UP showed plateaus near 2.5 V versus Li⁺/Li for both lithiation and delithiation with high Coulombic efficiency (ca. 100%), which is consistent with parent PTCDA (Figure 3a–d). The voltage range for insertion and deinsertion of Li ion was chosen based on the known mechanism for carbonyl groups as active centers for lithiation/delithiation (Figure S2, Supporting Information), projecting these materials as positive electrodes for rechargeable lithium batteries.^{20,29} The galvanostatic data for PTCDA (Figure 3a) are consistent with the reported values.²⁰ While PTCDA and UP samples showed flat, well-defined plateaus (Figure 3a,d), EDP showed a rather sloppy curve with a wider potential range (Figure 3b). Surprisingly, HP showed a distinct

discharge profile with a double plateau at 2.7 and 2.3 V Li⁺/Li, respectively (Figure 3c). Cyclic voltammetry studies were carried out to measure the reversibility of the positive electrodes by scanning the potential between 1.5 and 3.5 V versus Li⁺/Li at a scan rate of 0.02 mV/s. The first two cycles of cyclic voltammograms for PTCDA, EDP, and UP electrodes showed similar features during lithiation and delithiation (Figure 4a,b,d). CV curve for EDP showed a broad potential range for the lithiation and delithiation processes (Figure 4b), while multiple peaks have been observed in the CV data for HP (Figure 4c), in agreement with galvanostatic cycling profiles. A larger number of CV peaks and double-discharge plateau, as observed for HP electrode, could be due to the multiple steps through which lithiation and delithiation processes take place,²³ which could be further attributed to the inhomogeneity in the crystalline growth.

The capacity retention was studied at 50 mA g⁻¹ (Figure 3e), and the electrodes exhibited different cycling profiles. While EDP, HP, and UP polymers showed excellent capacity retention upon galvanostatic cycling up to 50 cycles, PTCDA showed rapid decay in the capacity after few initial cycles. It is interesting to note the superior performance of UP, which showed a gradual increase in the capacity in the initial cycles (initial capacity of 80 mA h g⁻¹) and got stabilized with a high lithiation capacity of 130 mA h g⁻¹ in 50 cycles. A much higher lithiation capacity of 165 mA h g⁻¹ has been achieved for UP in 50 cycles, cycled at a lower current rate of 20 mA g⁻¹ (Figure S3, Supporting Information). Upon lithiation, FT-IR spectrum of UP (Figure S4, Supporting Information) showed a new peak at 530 cm⁻¹ corresponding to lithiated carbonyl unit, as previously reported.³¹ HP also showed better cycling performance with an initial capacity of 130 mA h g⁻¹ and good capacity retention of 84.6% (110 mA h g⁻¹) over 50 cycles (Figure S3a, Supporting Information). While EDP retained 88.2% of the

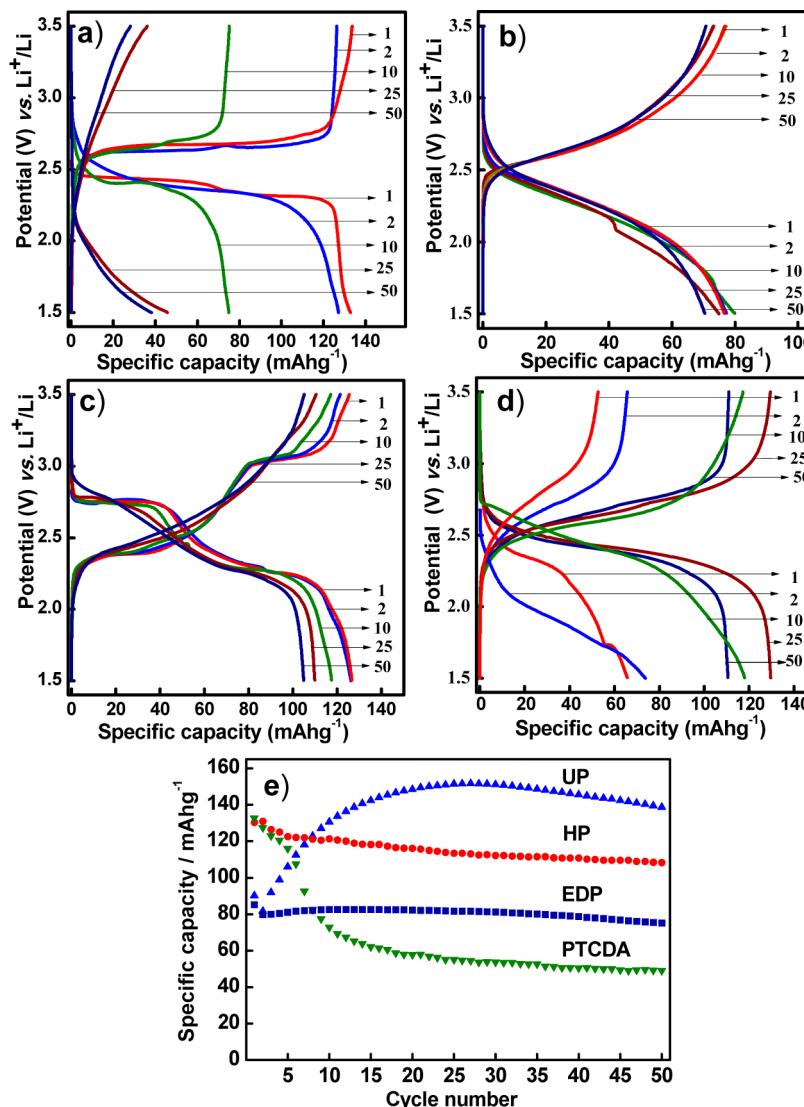


Figure 3. Voltage profiles of (a) PTCDA, (b) EDP, (c) HP, and (d) UP cycled at a current density of 50 mAhg⁻¹ in a voltage range of 1.5–3.5 V versus Li⁺/Li. (e) Cycling performance of PTCDA, EDP, HP and UP galvanostatically cycled between 1.5 and 3.5 V versus Li⁺/Li at a current density of 50 mAhg⁻¹.

initial capacity (85 mAhg⁻¹) over 50 cycles (Figure S3c, Supporting Information), PTCDA electrode exhibited low capacity retention of 37% of its initial capacity (132 mAhg⁻¹). Low capacity of EDP can be attributed to the ethylene bridge that contributes to the electrochemically silent domain. The present study thus highlights, an ingenious design of organic-based electrodes, with reduced electrochemical dead matter, as in the case of HP, and incorporation of an additional carbonyl group as an active site for the reversible Li uptake, as in the case of UP. Rate capability measurements have been performed for all electrodes by cycling at different current rates (Figure S3d, Supporting Information). HP and UP electrodes showed excellent power capability compared with EDP (Table S1, Supporting Information). The extended conjugation resulting from the polymerization of PTCDA is assumed to have improved the conductivity of these electrodes, leading to better rate capabilities. However, EDP showed poor performance, which completely decayed at higher current rates. Ethylene bridge inserted between the perylene diimide units could hinder the electron transport across the polymer backbone.

The mechanism of lithiation/delithiation processes in HP, EDP, and UP involves sequential structural rearrangements via enolization following a multiple lithiation, as reported.²⁹ Observed gradual increase in the capacity of UP with increasing cycles at various current rates could be attributed to stepwise insertion of Li ions in the imidic carbonyl, followed by urea carbonyl. Upon cycling, PTCDA showed an increase in impedance, as expected.

However, during the stepwise lithiation process, the effective impedance of the electrodes fabricated using UP decreases, resulting in improved electrochemical performance, which is confirmed from EIS studies (Figure 5). Increase in the electronic conductivity is shown to have improved the cyclic stability of UP. Combined beneficial properties arising from (i) favorable band gap for PTCDA core and (ii) insolubility of PTCDA-based polymers offset lower theoretical capacity of PTCDA, leading to an excellent organic electrode material (Table S1, Supporting Information).

To conclude, organic-based materials with carbonyl groups as reversible redox active centers have been designed, synthesized, and studied as positive electrodes in rechargeable lithium

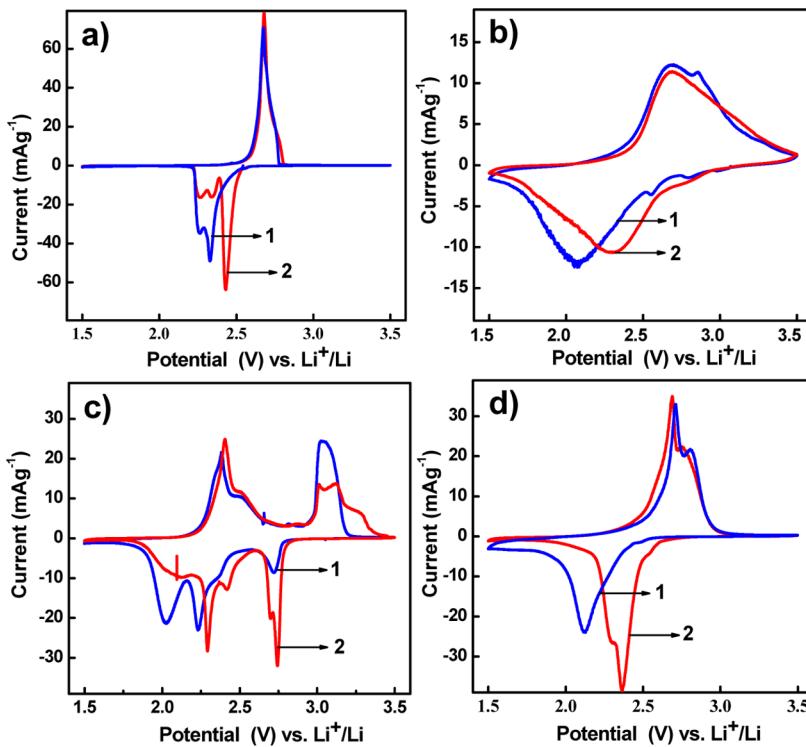


Figure 4. Cyclic voltammograms of (a) PTCDA, (b) EDP, (c) HP, and (d) UP within a potential range of 1.5–3.5 V versus Li^+/Li at a scan rate of 0.02 mVs^{-1} .

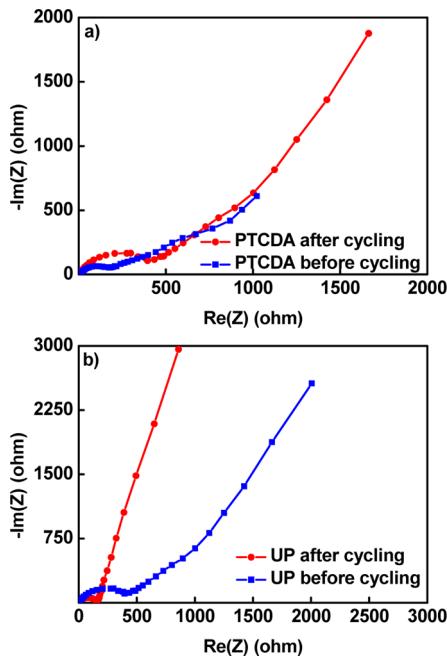


Figure 5. Electrochemical impedance spectra of (a) PTCDA and (b) UP. Impedance spectra have been recorded before cycling and after 100 cycles of charge discharge at 200 mA g^{-1} for each of the samples.

batteries. Different polyimides of PTCDA using ethylenediamine, hydrazine, and urea have been studied. Polyimidization of PTCDA has resulted in improved performance of the electrodes. Excellent electrochemical performance of UP electrode in terms of capacity, cyclic stability, and rate capability could be attributed to the presence of additional carbonyl group and enhanced conductivity upon cycling. The importance of

designing a new class of polymers having additional carbonyl functionalities with stable and efficient redox-active centers is highlighted using detailed electrochemical studies. Our work suggests that high-performance organic-based electrodes can be designed efficiently by polyimidization following a simple process, thus making it a potential alternative material for “greener and sustainable” electrochemical storage devices.

■ EXPERIMENTAL METHODS

Detailed synthesis procedure is given in the Supporting Information. Perylene polyimides obtained were characterized using various spectroscopic and analytical techniques viz. FT-IR spectroscopy, CP-MAS NMR spectroscopy, CHN elemental analysis, scanning electron microscopy, powder X-ray diffraction, thermogravimetric analysis, and so on. All of the polyimides were insoluble in common organic solvents for solution NMR. A solid-state ^{13}C MAS NMR measurement was performed on a Bruker Avance 400 (400 MHz) spectrometer with a MAS rate of 5 kHz. To record the SEM image of the samples, finely powdered samples were dispersed in ethanol and dropcasted on conductive carbon tape, and SEM images were recorded on a Nova NanoSEM450 FEI scanning electron microscope working at variable voltages from 10 to 30 kV, depending on the dimensions of the samples. Powder XRD for all of the samples were taken using Emperean, PANalytical instrument with reference radiation of $\text{Cu K}\alpha = 1.540 \text{ \AA}$ in the range 10–60°. IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR spectrometer as KBr pellets in all cases. CHN analyses were carried out on an Elementar vario MICRO cube elemental analyzer. SDT Q600 Thermogravimetric analyzer (TA Instruments) was used for the characterization of thermal stability of polyimides.

■ ASSOCIATED CONTENT

§ Supporting Information

Details of experimental procedures, elemental analysis, thermogravimetric analysis, power capability studies, and FT-IR spectrum of lithiated UP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

■ ACKNOWLEDGMENTS

We thank Ms. Shyama R. for the theoretical calculations. P.S. acknowledges the Department of Science and Technology for the INSPIRE scholarship. D.D. and K.N. acknowledge CSIR, Govt. of India, for the research fellowship. M.M.S. acknowledges Department of Science and Technology (DST), Govt. of India, for partial support of this work through DST Fast-track scheme for Young Scientists. M.H. acknowledges the Science and Engineering Research Board, SERB/F/0962, for the partial financial support of this work.

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