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An Organic Solvent-free Approach towards PDI/Carbon Cloth Composites as Flexible Lithium Ion Battery Cathodes

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Electronic Supplementary Information

Abstract An acidic solution based method towards flexible lithium ion battery (LIB) cathodes is developed in this work with perylene diimide (PDI) as the electroactive component and carbon cloth (CC) as the current collector. In this approach, PDI is firstly dispersed in concentrated sulfuric acid (H₂SO₄) and then deposited on CC substrate after the dilution of H₂SO₄, which provides an organic solvent-free strategy to construct integrated LIB cathodes. The acidic solution based fabrication process also allows the facile adjusting of loading amounts of PDI in the cathodes, which can effectively influence the battery performances of the PDI/CC cathodes. As the result, the acidic solution processed PDI/CC cathode can deliver a high specific capacity of ~ 36 mAh·g⁻¹ at the current density of 50 mA·g⁻¹ in both half cell with lithium foil as anode and full cell with prelithiated CC as anode. In both types of the batteries, the PDI/CC cathodes show good cycling stabilities by retaining ~ 84% of the initial capacities after 300 charge-discharge cycles at 500 mA·g⁻¹. Additionally, the excellent mechanical stability of the PDI/CC cathode enables the LIBs in pouch cell to maintain the electrochemical performances under various bending states, demonstrating their potentials for flexible LIBs.

Keywords Acidic solution processing; Perylene diimide; Carbon clothes; Organic cathodes; Flexible lithium ion batteries

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INTRODUCTION

Lithium ion batteries (LIBs) have been deeply involved in modern life by powering our cell-phones, laptops, cars, drones, and even toothbrushes.^[1–3] However, the foreseeable threat caused by people's increasing reliance on LIBs is not just the depletion of finite mineral resources for LIB electrodes such as lithium and cobalt, which could be relieved by developing the alternative electrodes^[4–6] or batteries^[7–11] with naturally abundant materials. In contrast, there is still no clear answer on the disposal of LIBs when they wear out.^[12,13] Not only do the waste LIBs have a high risk of fire or explosion if damaged, but the extraction of the inorganic ingredients in the batteries requires harsh conditions, which would lead to hazardous environmental impacts such as water and air pollutions.^[14–16]

In commercial LIBs, ~ 90% of the material cost and ~ 25% of the battery weight are contributed by their cathodes. Replacing the inorganic species in present LIB cathodes with electroactive organic compounds is an appealing solution to-

wards the aforementioned problems.^[17,18] The major elements of organic molecules are carbon, hydrogen, oxygen, and nitrogen, which are neither scarce nor expensive. Compared with their inorganic counterparts, the decomposition and recycling of organic materials are more simple and efficient.^[19–21] Additionally, organic LIB materials also have intriguing features including molecular-level tuneable electrochemical properties and high mechanical flexibility, rendering the design and fabrication of flexible or stretchable LIBs.^[22,23] However, the processing of the organic materials is often associated with the usage of large amounts of volatile solvent, which may become a new pollution source in the industrial-scale production.^[22,24–26] Considering the environmental impacts of both inorganic and organic materials in LIBs, the fabrication strategy of organic cathodes without organic solvents would hold a high potential for practical applications.

Herein, we report an acidic solution based processing method for fabricating the integrated organic LIB cathodes with 3,4,9,10-perylenetetracarboxylic diimide (peryene diimide or PDI) as the electroactive component, carbon cloth (CC) as the current collector, and concentrated sulfuric acid (H₂SO₄, 98%) as the solvent. All the ingredients in this method are commercially available and metal free, and the whole

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fabrication process does not require any organic solvent. The concentrated H_2SO_4 allows the effective dispersion of PDI and the subsequent dilution of the acidic suspension renders the deposition of PDI with adjustable ratios on the CC substrates. The resultant PDI/CC cathodes manifest excellent performances in half cell with lithium foil anode and full cell with pre-lithiated carbon cloth anode including a high specific capacity of $\sim 136 \text{ mAh}\cdot\text{g}^{-1}$ at the current density of $50 \text{ mA}\cdot\text{g}^{-1}$ and a high cycling stability with $\sim 84\%$ retention rate of the initial capacity after 300 charge-discharge cycles at $500 \text{ mA}\cdot\text{g}^{-1}$. More importantly, the outstanding lithium storage behavior of PDI/CC cathode can also be reserved in pouch cells under different bending states, confirming the advantages of the acidic solution processed organic cathodes in flexible LIBs.

EXPERIMENTAL

Materials

3,4,9,10-Perylenetetracarboxylic diimide (perylene diimide or PDI, 95%) was obtained from Shanghai J&K Chemical Technology Co., Ltd. Carbon black (Super P) was provided by Shanghai Xiaoyuan Energy Technology Co., Ltd. Concentrated sulfuric acid (H_2SO_4 , 98%) and *N*-methyl-2-pyrrolidone (NMP) were bought from Shanghai Tansoo Scientific Co., Ltd. Carbon cloth (CC, W0S1009) was purchased from Suzhou Yilongshen Energy Technology Co., Ltd. All the chemicals were of analytical grades and used as received without further purification.

Preparation of the PDI/CC Cathodes

Carbon cloth was washed with ethanol and acetone and then dried under vacuum at 100°C for 12 h. On the other hand, the mixture of PDI (90 wt%) and carbon black (10 wt%) was dispersed in concentrated H_2SO_4 with magnetic stirring to form the homogeneous suspensions. To optimize the loading amount of PDI in the PDI/CC cathodes, three suspensions with different concentrations of the solid contents (PDI + carbon black = 20, 30, and $40 \text{ mg}\cdot\text{mL}^{-1}$) were prepared. Subsequently, the CC substrates were dipped in the suspensions for 5 min and then immersed in deionized water for several times to remove the residue H_2SO_4 and allow the deposition of PDI. Next, the samples were vacuum dried at 100°C for 12 h to generate the integrated PDI/CC cathodes. According to the concentrations of the suspensions, the cathodes were named as PDI/CC-1 ($20 \text{ mg}\cdot\text{mL}^{-1}$), PDI/CC-2 ($30 \text{ mg}\cdot\text{mL}^{-1}$), and PDI/CC-3 ($40 \text{ mg}\cdot\text{mL}^{-1}$), respectively.

In controlled experiments, an *N*-methyl-2-pyrrolidone (NMP) suspension of PDI (90 wt%) and carbon black (10 wt%) with a total solid content of $20 \text{ mg}\cdot\text{mL}^{-1}$ was prepared by ultra-sonication for 30 min. The CCs were immersed in the suspension for 5 min and then washed with deionized water for several times. After dried under vacuum at 100°C for 12 h, the sample noted as PDI/CC-N was obtained.

Preparation of PDI-A and PDI-N

PDI was dissolved in concentrated H_2SO_4 to form a homogeneous suspension with the concentration of $20 \text{ mg}\cdot\text{mL}^{-1}$. After stirred for 30 min, the PDI suspension was poured into ice water (100 mL), which caused the precipitation of PDI from the diluted H_2SO_4 . Subsequently, the precipitate was filtered, washed with deionized water for several times, and vacuum dried at 100°C for 12 h to produce PDI-A.

Similarly, PDI was dispersed in NMP with the concentration of $20 \text{ mg}\cdot\text{mL}^{-1}$ by ultra-sonication for 30 min. After that, PDI was filtered from the dispersion and vacuum dried at 100°C for 12 h to produce PDI-N.

Structure Determinations

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of the PDI/CC cathodes were measured on a NEXUS 670 spectrometer. The Fourier transform infrared spectra (FTIR) of the powder-like samples were recorded with a Nicolet 6700 spectrometer by pressing into pellets with KBr. The crystallization degree of the samples was investigated by powder X-Ray diffraction (XRD, Rigaku D/Max 2500) with Cu $K\alpha$ irradiation ($\lambda = 1.54 \text{ \AA}$) at a scanning rate of $5^\circ\cdot\text{min}^{-1}$. The morphologies of the samples were characterized by scanning electron microscopy (SEM, JEOL JSM-7800F Prime, 5 kV). The Raman spectroscopy was performed on a Dispersive Raman Microscope (Senterra R200-L) with an Ar-ion laser excitation at 785 nm with a power of about 100 mW.

Electrochemical Measurements

The electrochemical performances of the PDI/CC cathodes in half cells were measured in 2016 coin-type cells with PDI/CC as the cathode and lithium foil as the anode. The electrolyte was LiPF_6 ($1 \text{ mol}\cdot\text{L}^{-1}$) in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1:1:1, V:V:V), and the separator was polypropylene (Celgard 2400). The batteries were assembled in an argon-filled glove box with the moisture and oxygen concentrations below 1 ppm. The cyclic voltammetry (CV) profiles of the samples were measured on a CHI760e electrochemical workstation at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$. The galvanostatic charge-discharge (GCD) tests were conducted on Land CT2001A testing system in the potential range of 1.5 V to 3.5 V. The specific capacities were calculated with the mass of PDI in the cathode. Electrochemical impedance spectroscopy (EIS) was performed on the CHI760e electrochemical workstation with an amplitude of 5 mV over the frequency range from 0.01 Hz to 100000 Hz.

The electrochemical performances of the full cell were measured in both 2032 type coin cells and aluminum laminated film wrapped pouch cells with PDI/CC-1 as the cathode, pre-lithiated carbon cloth (CC) as the anode, LiPF_6 ($1 \text{ mol}\cdot\text{L}^{-1}$) in EC:DMC:EMC (1:1:1, V:V:V) as the electrolyte, and polypropylene (Celgard 2400) as the separator. The pre-lithiation of the CC anodes was performed through an internal short approach. Typically, electrolyte was dropped on the CC anode, and then a lithium foil was put on it. The CC and lithium foil were pressed by glass plates for 120 min to complete the pre-lithiation process. The sizes of the electrodes in pouch cells were $2 \text{ cm} \times 3 \text{ cm}$. And the pouch cells were sealed by a vacuum heat sealing machine. The pre-lithiation process and the assembling of the batteries were all performed in an argon-filled glove box with the moisture and oxygen concentrations below 1 ppm. The galvanostatic charge-discharge (GCD) tests of the full cell were carried out with a Land CT2001A testing system in the potential range of 1.5 V to 3.0 V. The cell capacity was calculated based on the mass of PDI in the cathode. The CV profiles of the full cell were measured by a CHI760e electrochemical workstation at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$.

RESULTS AND DISCUSSION

The fabrication process for the PDI/CC cathodes is illustrated in Fig. 1. Firstly, the mixture of PDI and carbon black with a mass ratio of 9:1 was dispersed in concentrated H_2SO_4 . In this step, the protonation of PDI renders the good dispersibility of positively charged PDI in H_2SO_4 ,^[27–30] thus leading to the homogeneous suspensions. Herein, PDI is selected as the electroactive component due to its high electrochemical activity and good stability.^[19] Many researchers have managed to develop PDI based cathode materials for LIBs.^[29–33] For instance, Krishnamoorthy *et al.* treated carboxylic acid containing PDI with hydrazine. The reduced PDI manifested a high capacity of $\sim 100 \text{ mAh}\cdot\text{g}^{-1}$ at the charging rate of 20 C.^[31] Seferos' group synthesized a three-dimensional framework of triptycene and PDI. As the organic cathode of LIBs, the PDI-triptycene framework could deliver a capacity of $\sim 76 \text{ mAh}\cdot\text{g}^{-1}$ at 0.05 C.^[32] Recently, Ramanujam and co-worker examined the electrochemical performance of glyciny substituted PDI as LIB cathode, which retained 70% of the theoretical capacity ($110 \text{ mAh}\cdot\text{g}^{-1}$) after 2000 charge-discharge cycles.^[33] On the other hand, the addition of carbon black is to reduce the resistance within the resulting PDI/CC cathodes. Subsequently, a piece of CC was dipped in the suspensions for 5 min to allow the sufficient adsorption of PDI and carbon black on the surface of CC via the aromatic and hydrophobic interactions between them. After that, the CC was transferred to deionized water to remove the residue H_2SO_4 . With the dilution and departure of the acid, deprotonated PDI would form a stable layer on the CC substrate, which therefore generated the PDI/CC cathodes. In the whole fabrication process, concentrated H_2SO_4 only acted as the solvent and no reaction happened except its dilution. Without high temperature, high pressure or volatile solvents, our method provides a low cost and environmentally friendly strategy to construct organic LIB cathodes. To find the optimized loading amount of PDI in the cathodes, three suspensions with different concentrations of the solid contents (PDI + carbon black = 20, 30 and $40 \text{ mg}\cdot\text{mL}^{-1}$) were prepared in this work. Accordingly, the resulting cathodes were noted as PDI/CC-1 (from the suspension with the concentration of $20 \text{ mg}\cdot\text{mL}^{-1}$), PDI/CC-2 ($30 \text{ mg}\cdot\text{mL}^{-1}$), and PDI/CC-3 ($40 \text{ mg}\cdot\text{mL}^{-1}$). In controlled experiments, a reference sample named as PDI/CC-N was fabricated by soaking the CC substrate in the NMP dispersion of

PDI and carbon black with the concentration of $20 \text{ mg}\cdot\text{mL}^{-1}$ (PDI:carbon black = 9:1). Additionally, to elucidate the influence of solvents on the morphology of PDI, two PDI samples were further prepared by dispersing PDI in concentrated H_2SO_4 and NMP, which were then named as PDI-A and PDI-N, respectively (the electronic supplementary information, ESI).

The amount of PDI in the resulting PDI/CC cathodes can be easily determined by checking the weight variations of the CCs after the acid assisted fabrication process. As summarized in Table S1 (in ESI), the loading ratios of PDI in PDI/CC-1, PDI/CC-2, and PDI/CC-3 show an obvious upward trend with the increased concentrations of H_2SO_4 suspensions. In contrast, the amount of PDI in PDI/CC-N is almost 2.5 times higher than that of PDI/CC-1 and close to the value in PDI/CC-2. The PDI concentrations and solvents of the suspensions do not only influence the loading ratios of PDI in the PDI/CC cathodes. The surface morphology of these cathodes also has obvious relevance with the processing conditions, which can be evidenced by their scanning electron microscopy (SEM) images. As shown in Fig. S1 (in ESI), the pristine CC substrates are composed by bundles of carbon fibers with the diameter of $\sim 10 \mu\text{m}$ and each fiber has a relatively smooth surface with a few thread-like shallow grooves along the axial direction. Differently, a layer of PDI can be found in all of the PDI/CC cathodes (Fig. 2 and Fig. S2 in ESI). In the case of PDI/CC-1, the PDI layer is homogeneously deposited on the surface of CC substrates (Figs. 2a and 2b). Some particles with the sizes of $\sim 100 \text{ nm}$ are decorated within the PDI film, which should be the carbon black. Not like the typical rod-like pristine PDI (Fig. S3a in ESI), the PDI particles in PDI/CC-1 are fused together with vague boundaries, which are similar to those in PDI-A (Fig. S3b in ESI). This kind of morphology can be attributed to the dissolution of PDI in H_2SO_4 ,^[30] which is not observable in the samples treated with NMP. As displayed by Fig. S2 (in ESI), PDI on the surface of PDI/CC-N forms a rough film and still reserves the rod-like structure as the pristine PDI. A similar situation can also be found in the SEM image of PDI-N (Fig. S3c in ESI), implying the different roles of H_2SO_4 and NMP in the fabrication processes. Except for the solvent, the PDI concentrations of the acidic dispersions can also influence the morphology of the PDI/CC cathodes. As shown in the SEM images of PDI/CC-2, a condense PDI film with crumbles is wrapped around the CC substrates (Figs. 2c and 2d). And large agglomerations of PDI with disordered shapes can be found in PDI/CC-3 (Figs. 2e and 2f), which is due to the highest loading ratio of PDI in the cathode.

To further explore the composition and structure of the PDI/CC cathodes, the Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) patterns of the samples are compared in this work (Fig. 3). To avoid the interference of CC substrates in the cathodes, the FTIR and XRD spectra of pristine PDI, PDI-A, and PDI-N are also recorded. In the FTIR spectra of pristine PDI (Fig. 3a), the absorption bands at 1687 , 1362 , and 3154 cm^{-1} can be ascribed to the stretching vibrations of the $\text{C}=\text{O}$, $\text{C}-\text{N}$, and $\text{N}-\text{H}$ bonds in the imide groups of PDI. And the bands at 3044 , 2919 , 2856 , and 1588 cm^{-1} can be assigned to the stretching vibrations of aromatic $\text{C}-\text{H}$ bonds and perylene ring.^[34,35] The pristine PDI, PDI-A, and PDI-N manifest almost identical FTIR spectra, suggesting that

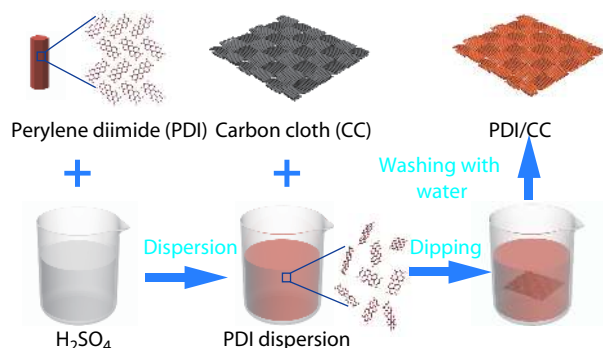


Fig. 1 The schematic illustration on the acidic solution based processing method towards the integrated PDI/CC cathodes in this work.

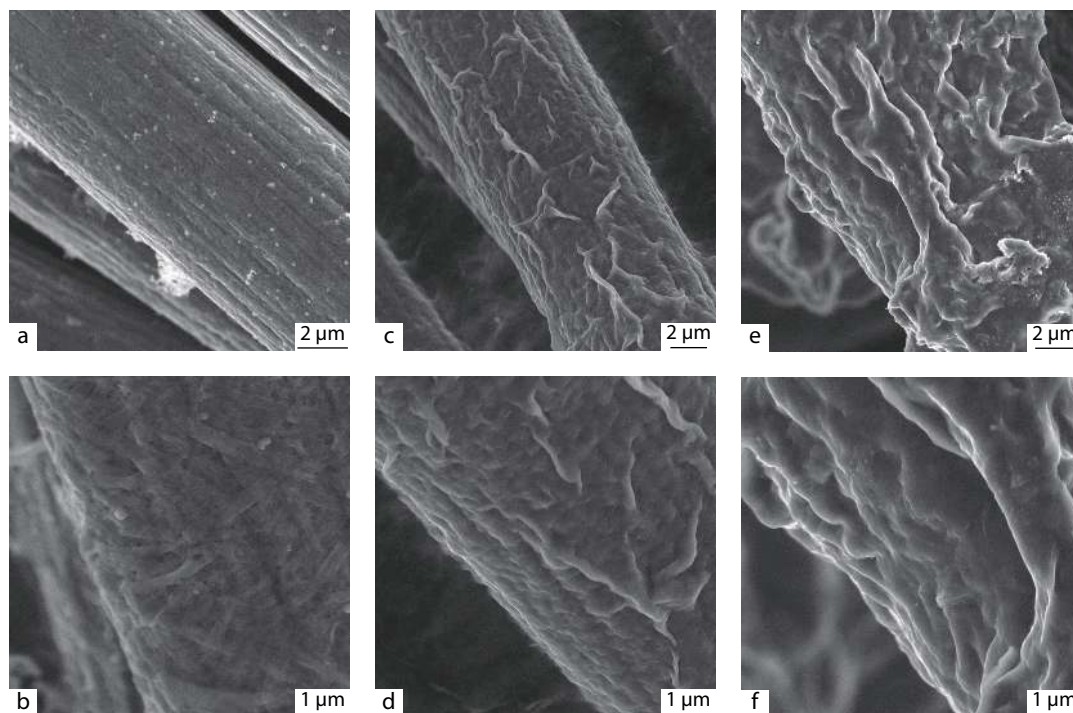


Fig. 2 SEM images of the acidic solution processed PDI/CC composites. (a, b) PDI/CC-1, (c, d) PDI/CC-2, (e, f) PDI/CC-3.

the different solution processing has no influence on the chemical structure of PDI. Similarly, the PDI/CC cathodes also have very closed FTIR profiles with only differences in the intensities of the absorptions (Fig. 3b), which all belong to the characterized absorption bands of PDI, confirming that the acidic solution based fabrication procedures are simple physical processes and no chemical reactions are involved. On the other hand, the XRD patterns of pristine PDI have distinct diffraction peaks at 10° , 12° , 20° , 25° , 27° , and 30° (Fig. 3c), which can be ascribed to the (011), (021), (002), $(11\bar{2})$, $(12\bar{2})$, and (140) planes of the monoclinic $P21/n$ space group, respectively.^[35] The similar diffractions can still be found in the XRD profiles of PDI-N, only with a slight shift to the smaller 2θ values, implying larger intermolecular distances.^[36,37] In the case of PDI-A, the intensities of many diffraction peaks are greatly depressed and their positions shift to larger 2θ values, suggesting that the PDI molecules in PDI-A have a reduced crystalline degree but enhanced intermolecular distances. Different from their FTIR results, the XRD patterns of PDI-A and PDI-N have obvious differences, attributable to the different effects of the solvents.^[29,30] In contrast, the PDI/CC cathodes have similar XRD patterns with one distinct peak at $\sim 25^\circ$ and multiple weak peaks in the range of 12° – 30° (Fig. 3d). The strong and broad peak is ascribable to the (002) reflections of the graphitic carbon,^[38] which should be derived from the CC substrate and the aromatic interactions between PDI and CC.

To evaluate the electrochemical performances of the PDI/CC cathodes, their cyclic voltammetry (CV) profiles were recorded in coin-type half cells with lithium foil as the anode in the voltage range of 1.5 V to 3.5 V at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$ (Fig. 4a). In the cathodic scan, PDI/CC-1 exhibits a distinct reduction peak at 2.26 V and a much weaker peak at 2.50 V. Correspondingly, two oxidation peaks at 2.71 and

2.76 V can be found in its anodic scan. The similar redox couples at $\sim 2.26/2.50 \text{ V}$ and $\sim 2.71/2.76 \text{ V}$ can be found in the CV curves of PDI/CC-2 and PDI/CC-3, respectively. The current densities of the three PDI/CC cathodes are gradually increased, which should be due to the different loading amounts of PDI in them.^[22,39] In contrast, the CV profile of PDI/CC-N only contains one pair of redox peaks at 2.25 and 2.74 V without fine structure. Moreover, the intensities of these peaks are much lower than those in PDI/CC-2 although they have similar amount of PDI, which might be caused by the difference in their conductivities.^[40,41] According to previous literature, the electrochemical reaction of PDI with lithium ions in this voltage range involves the transportation of two electrons (Scheme S1 in ESI), corresponding to a theoretical specific capacity of $\sim 137 \text{ mAh}\cdot\text{g}^{-1}$.^[42,43] On the other hand, the galvanostatic charge-discharge (GCD) profiles of the PDI/CC cathodes at a current density of $50 \text{ mA}\cdot\text{g}^{-1}$ indicate that all of the samples have an obvious charge/discharge plateau at about 2.60/2.40 V versus Li/Li^+ (Fig. 4b), which are in good agreement with their CV curves.

Based on the results from the GCD tests at varied charge-discharge current densities from $50 \text{ mA}\cdot\text{g}^{-1}$ to $2000 \text{ mA}\cdot\text{g}^{-1}$, the rate capabilities of the PDI/CC cathodes are summarized in Fig. 4(c). It is notable that PDI/CC-1 delivers a high specific capacity of $136 \text{ mAh}\cdot\text{g}^{-1}$ at $50 \text{ mA}\cdot\text{g}^{-1}$, closing to the theoretical value of PDI, while the specific capacities of PDI/CC-2 and PDI/CC-3 are only 113 and $66 \text{ mAh}\cdot\text{g}^{-1}$, respectively. Even at a high current density of $2000 \text{ mA}\cdot\text{g}^{-1}$, the capacity of PDI/CC-1 still can be retained at $118 \text{ mAh}\cdot\text{g}^{-1}$, much higher than those of PDI/CC-2 ($92 \text{ mAh}\cdot\text{g}^{-1}$) and PDI/CC-3 ($44 \text{ mAh}\cdot\text{g}^{-1}$). Obviously, with the increased loading amounts of PDI, the capacities of the acidic solution processed PDI/CC cathodes have a downward trend along with the increasing loading amount of

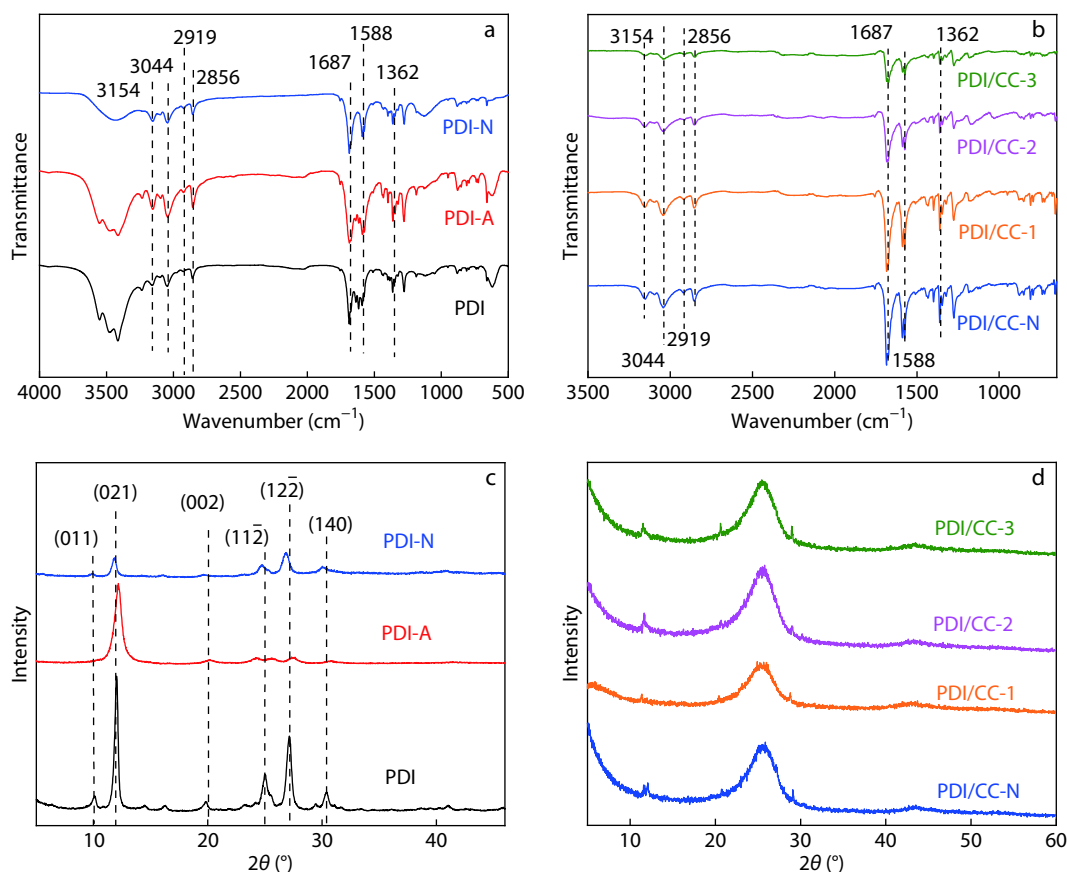


Fig. 3 (a) FTIR spectra of pristine PDI, PDI-A, and PDI-N. (b) FTIR spectra of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N. (c) XRD patterns of pristine PDI, PDI-A, and PDI-N. (d) XRD patterns of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N.

PDI, which can be correlated with their morphology from the SEM characterization. With the moderate ratio of PDI in PDI/CC-1, the PDI component can form a homogenous layer over the CC substrate without aggregation, which allows efficient transportation of charge carriers within the whole cathode.

In the case of PDI/CC-2 and PDI/CC-3, the electrolyte cannot fully access the aggregated PDI, thus leading to the drastically decreased specific capacity.^[44] Except the amount of PDI, the fabrication methods also show profound impacts on the electrochemical performances of the PDI/CC cathodes. As shown in Fig. 4(c), PDI/CC-N manifests a discharge capacity of $66 \text{ mAh}\cdot\text{g}^{-1}$ at $50 \text{ mA}\cdot\text{g}^{-1}$, which drops to $39 \text{ mAh}\cdot\text{g}^{-1}$ at $2000 \text{ mA}\cdot\text{g}^{-1}$. Given that PDI/CC-N has a similar loading amount of PDI to PDI/CC-2, its much reduced performances should be caused by the distinct morphology of the PDI layers in these cathodes. Besides the rate capabilities, the PDI/CC cathodes also exhibit different cycling stabilities (Fig. 4d). With the coulombic efficiencies (CEs) of 100%, the capacities of PDI/CC-1 vary from $126 \text{ mAh}\cdot\text{g}^{-1}$ to $106 \text{ mAh}\cdot\text{g}^{-1}$ after 300 charge-discharge cycles at a current density of $500 \text{ mA}\cdot\text{g}^{-1}$, corresponding to a high retention rate of 83%, which is similar to that of PDI/CC-2 (84%) and higher than those of PDI/CC-3 (75%) and PDI/CC-N (75%). The differences in the electrochemical performances of the PDI/CC cathodes should be due to the distinct combination effects of PDI and CC caused by the processing method as well as the amount of PDI.

An evidence about the different solvent effects can be found in the optical behavior of PDI in H_2SO_4 and NMP (Fig. S4 in ESI). PDI dispersed in H_2SO_4 exhibits strong red fluorescence under the irradiation of 365 nm UV light, while its NMP dispersion shows no fluorescence at all. The UV-Vis spectra of PDI in H_2SO_4 have four distinct absorption bands at 478, 513, 551, and 596 nm (Fig. S4b in ESI), which can be ascribed to the $0\rightarrow3$, $0\rightarrow2$, $0\rightarrow1$, and $0\rightarrow0$ vibronic $\pi\text{-}\pi^*$ transitions in PDI, respectively.^[45] Generally, the self-aggregation of PDI will cause the shift of absorption bands gradually from $0\rightarrow0$ to $0\rightarrow1$ and $0\rightarrow2$ transitions,^[46,47] which can perfectly explain the unresolved broad UV-Vis spectra of PDI in NMP with low intensity. In the fluorescence spectra (Fig. S4c in ESI), PDI in H_2SO_4 exhibits a maximum emission wavelength of 631 nm, which is typical for the well-dispersed PDI in solution. Under the same conditions, the emission wavelength of PDI in NMP blue-shifts to 420–550 nm, which should also be caused by the strong aggregation of PDI.^[45] Therefore, the acidic solution based processing is not a simple physical mixing of PDI with CC in the presence of solvent, but actually a dissolution-precipitation processes. The Raman spectra of the PDI/CC cathodes were further recorded to explore the local structures of PDI in them (Fig. S5 in ESI). In the case of pristine PDI, the bands at 242, 546, and 1066 cm^{-1} can be ascribed to the bending vibration of the C—N—C group, ring radial vibrations of perylene and C—H bending vibrations, respectively.

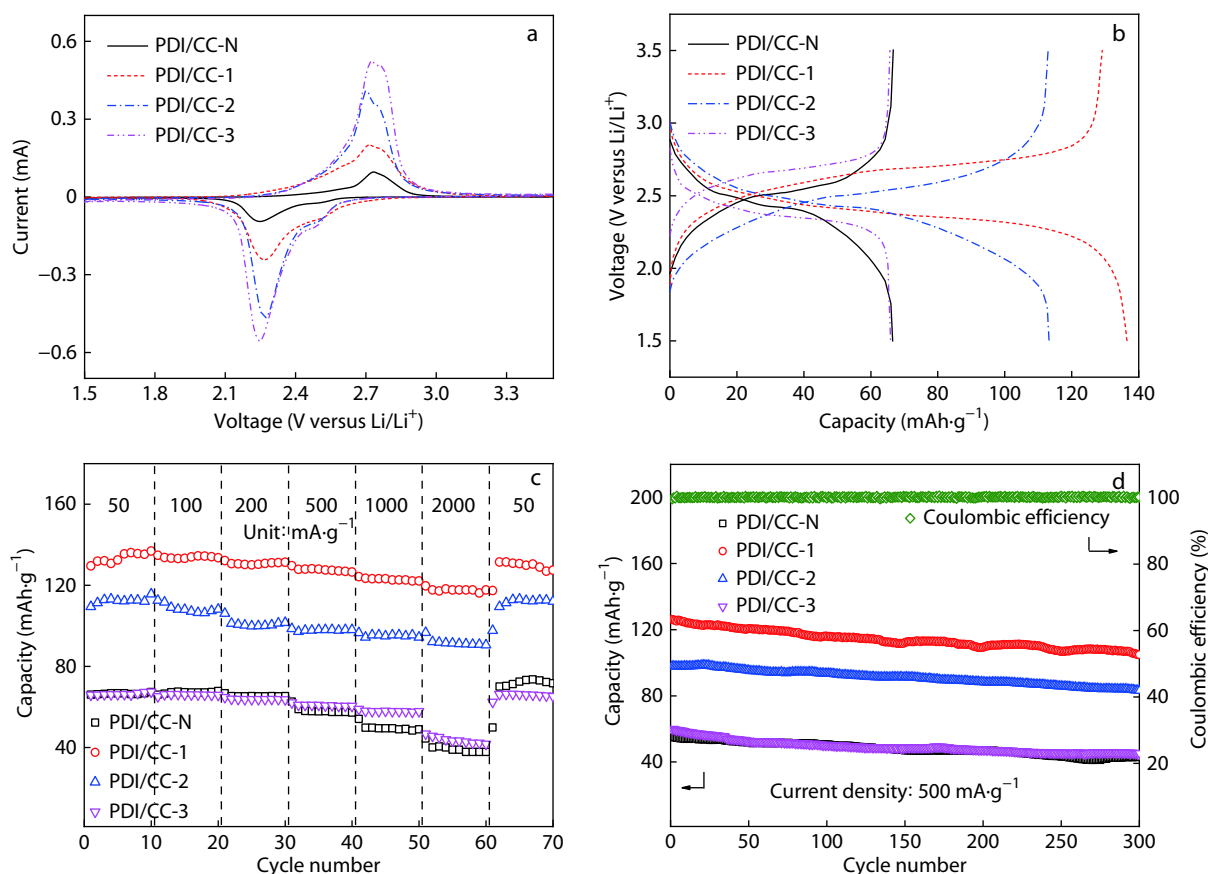


Fig. 4 Electrochemical characterization of the PDI/CC cathodes in half cells with lithium foil as the anode. (a) CV profiles of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N in the voltage range of 1.5 V to 3.5 V at a scan rate of 0.5 mV·s⁻¹. (b) GCD profiles of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N at a current density of 50 mA·g⁻¹; (c) Rate capabilities of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N with the current densities in the range of 50–2000 mA·g⁻¹. (d) Discharge capacities of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N at 500 mA·g⁻¹ for 300 charge-discharge cycles and the corresponding CEs of PDI/CC-1.

ely.^[48] And the bands at 1302, 1375, and 1444 cm⁻¹ are from the stretch of the conjugated ring, while the ones at 1571, 1612, and 1586 cm⁻¹ correspond to the C=C stretch vibrations.^[49,50] It is worth noting that the absorption bands from PDI in the Raman spectra of PDI/CC-N perfectly coincide with those of the pristine PDI, while the bands in the three acid-processed PDI/CC cathodes exhibit slight red-shifts. Basically, the Raman bands of a sample will shift to lower frequency when doped by electron donors.^[51] Since PDI is a typical electron acceptor, its deposition on the surface of electron-rich CC may result in the charge transfer between them. Therefore, the red-shifts in the Raman spectra of the acid processed PDI/CC cathodes suggest the improved combination effects of PDI and CC.

To further examine the contact between PDI and CC, electrochemical impedance spectra (EIS) of the PDI/CC cathodes were employed to reveal the reaction kinetics for the insertion/de-insertion of lithium ions in them (Fig. 5a). According to the inset equivalent circuit, the charge transfer resistances in the electrolyte/electrode interface (R_{ct}) of PDI/CC-1, PDI/CC-2, PDI/CC-3, and PDI/CC-N are 116.9, 169.6, 234.9 and 230.0 Ω , respectively. The values of R_{ct} from the acidic solution processed PDI/CC cathodes gradually increase in the sequence of PDI/CC-1, PDI/CC-2, and PDI/CC-3, and the vari-

ation trend is in good accordance with the amount of PDI, which explains their different rate capabilities.^[52,53] On the other hand, PDI-N has a high R_{ct} of 230.0 Ω , which is close to the value of PDI/CC-3 and much higher than that of PDI/CC-2, attributable to the different influences of the solvents. The galvanostatic intermittent titration technique (GITT) was further applied to compare the PDI/CC cathodes by using a current density of 10 mA·g⁻¹ with a charge-discharge intermittent of 1 h and a consequent relaxation time of 2 h (Fig. 5b). Under the conditions of the GITT test, PDI/CC-N, PDI/CC-1, PDI/CC-2, and PDI/CC-3 show discharged specific capacities of 61, 136, 111, and 96 mAh·g⁻¹, respectively. Compared with the values from GCD profiles (Fig. 4b), the capacities of PDI/CC-N, PDI/CC-1, and PDI/CC-2 are nearly unchanged, while that of PDI/CC-3 improves dramatically from 66 mAh·g⁻¹ to 96 mAh·g⁻¹. Therefore, the low capacity of PDI/CC-3 is mainly caused by the slow lithiation kinetics of the aggregated PDI layer,^[54,55] which is still accessible to the electrolyte. In contrast, large proportion of PDI in PDI/CC-N is inactive even under the conditions of GITT,^[56] suggesting the superiority of the acidic solution based processing method. Since PDI/CC-2 and PDI/CC-N have similar loading ratio of PDI, their GITT curves are further compared to elucidate the difference between H₂SO₄ and NMP. As shown in Fig. 5(c), PDI/CC-2 has

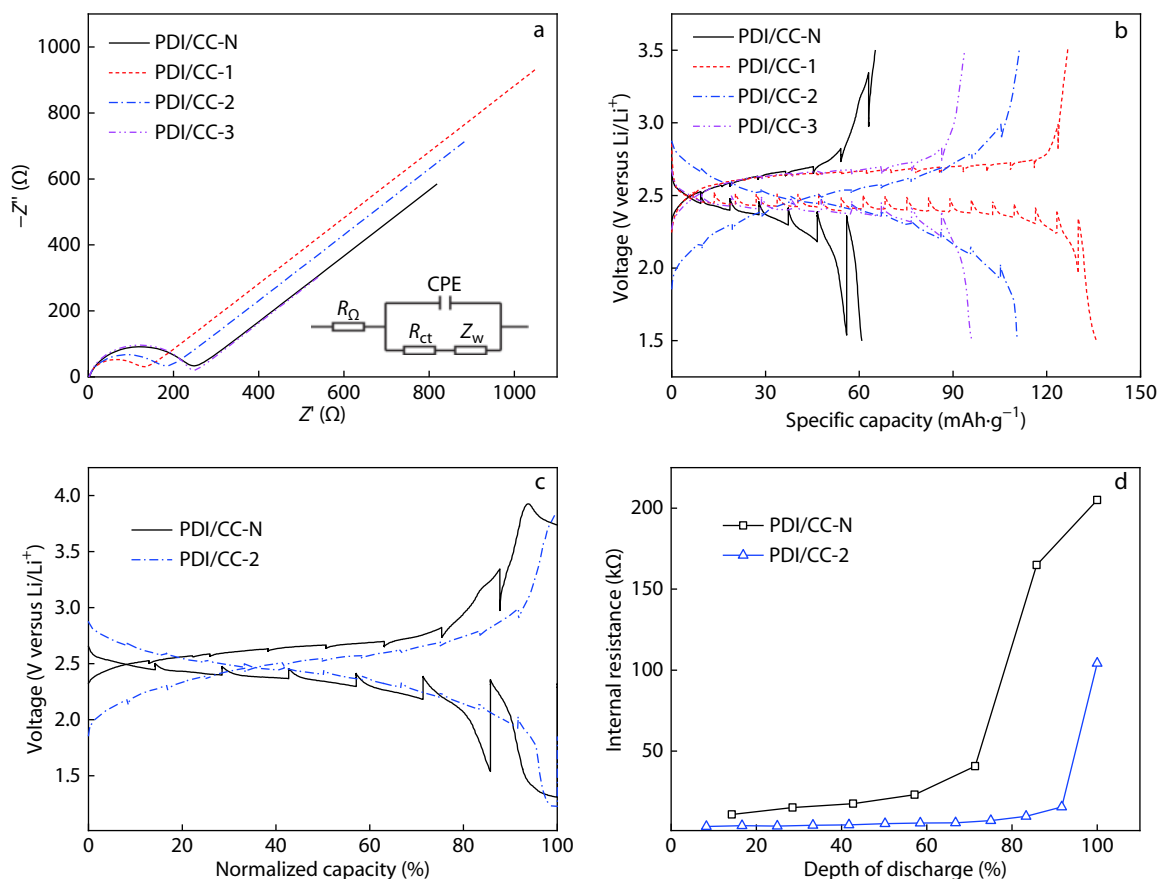


Fig. 5 (a) The electrochemical impedance profiles of the PDI/CC cathodes. The inset is an equivalent circuit for the analysis of R_{ct} . (b) GITT curves of the PDI/CC cathodes obtained in half cells at a current density of $10 \text{ mA}\cdot\text{g}^{-1}$ with a charge-discharge intermittent of 1 h and a consequent relaxation time of 2 h. (c) The comparison of the GITT profiles of PDI/CC-N and PDI/CC-2 with normalized capacity. (d) The internal resistances of PDI/CC-N and PDI/CC-2 as a function of the depth of discharge.

a more depressed cell polarization than PDI/CC-N with the normalized capacity. To quantify the cell polarization of both cathodes, the internal cell resistances of them were calculated in Fig. 5(d) as a function depth of discharge, which indicates the internal resistances of PDI/CC-2 are much lower than those of PDI/CC-N at any discharge states. Considering the results from the structural characterization, the acidic solution processing allows the fusion of PDI nanorods on the surface of CC, which can lead to the efficient combination of PDI and CC in the resulting cathodes, thus resulting in a better charge carrier mobility within PDI/CC-2 than PDI/CC-N.

With excellent electrochemical performances, the integrated PDI/CC cathodes were obtained in this work without tedious synthesis processes or post treatments,^[31–33] which is attributed to the advantages of the solution based fabrication method. Encouraged by the excellent performances of PDI/CC-1 in half cell, we further evaluated its lithium storage behavior as the cathode in full cell with pre-lithiated carbon cloth as the anode (Fig. 6a and Fig. S6 in ESI). Named as PDI/CC-1||CC, the full cell can have a capacity close to its theoretical value ($136 \text{ mAh}\cdot\text{g}^{-1}$) at the current density of $50 \text{ mA}\cdot\text{g}^{-1}$ (Fig. 6b), which is almost the same as the result from the half cell. More impressively, PDI/CC-1||CC still holds a high capacity of $102 \text{ mAh}\cdot\text{g}^{-1}$ even at an ultrahigh current

density of $5000 \text{ mA}\cdot\text{g}^{-1}$, revealing its excellent rate capability. On the other hand, the good cycling stability of PDI/CC-1 can also be retained in the full cell. As indicated in Fig. 6(c), PDI/CC-1||CC manifests a capacity of $101 \text{ mAh}\cdot\text{g}^{-1}$ after 300 charge-discharge cycles at $500 \text{ mA}\cdot\text{g}^{-1}$, corresponding to a high retention rate of 83% for its initial value ($120 \text{ mAh}\cdot\text{g}^{-1}$). Benefiting from the good mechanical stability of its electrodes, PDI/CC-1||CC can reserve its capacities at bending states, indicating another feature of the acidic solution processed cathodes. With the gradual variation of the bending angles of 0° , 90° , 180° , and $\text{Re-}0^\circ$ (restored to flat state), the capacities of PDI/CC-1||CC at $250 \text{ mA}\cdot\text{g}^{-1}$ are 133, 132, 130, and $129 \text{ mAh}\cdot\text{g}^{-1}$, respectively (Fig. 6d), which show no obvious changes at the different bending states. In addition, the GCD profiles of PDI/CC-1||CC under bending states further confirm the stable output voltages of the full cell (Fig. 6e). With a static bending angle of 90° , PDI/CC-1||CC can reserve 89% of the initial capacity with a quantitative CE after 200 charge-discharge cycles at $250 \text{ mA}\cdot\text{g}^{-1}$ (Fig. 6f). As summarized in Table S2 (in ESI), the electrochemical performances of PDI/CC-1||CC are comparable to recently reported full cells with either inorganic or organic electrodes, further demonstrating its appealing potential for the practical applications in flexible energy storage.

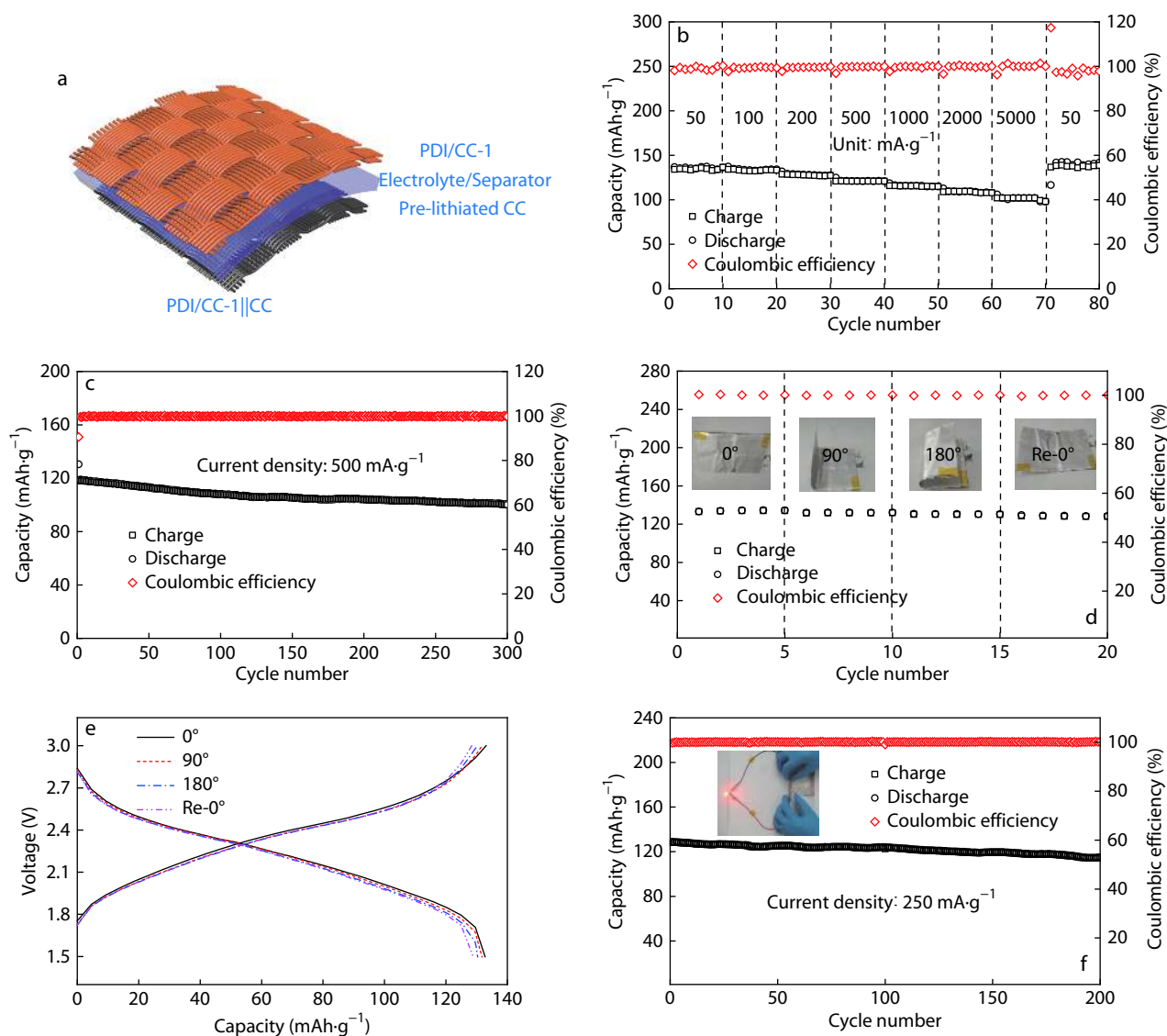


Fig. 6 (a) The schematic illustration on the structure of PDI/CC-1||CC. (b) Rate capabilities of PDI/CC-1||CC with current densities in the range of 50–5000 mA·g⁻¹. (c) The capacities and CEs of PDI/CC-1||CC at 500 mA·g⁻¹ for 300 charge-discharge cycles. (d) The capacities and CEs of PDI/CC-1||CC at the current density of 250 mA·g⁻¹ with different bending angles of 0°, 90°, 180°, and Re-0°. (e) GCD curves of PDI/CC-1||CC with different bending angles of 0°, 90°, 180°, and Re-0°. (f) The capacities and CEs of PDI/CC-1||CC at 250 mA·g⁻¹ for 200 charge-discharge cycles with the bending angle of 90°.

CONCLUSIONS

In this work, PDI and CC based LIB cathodes were prepared by an acidic solution assisted processing method, which can easily produce integrated cathodes with good electrochemical performances and high mechanical stability. The fabrication process needs neither organic solvents nor high temperatures, thus providing a simple and environmentally friendly avenue for organic LIB cathodes. Compared with the inorganic LIB cathodes, the PDI/CCs with low cost and high sustainability are more attractive considering the potential economic and environmental problems caused by the mineral components in present LIBs. Moreover, the general applicability of organic electrodes will also enable this method to be applied in the manufacturing of organic secondary battery cathodes with

diversified charge carriers including sodium, magnesium, and potassium.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2388-8>.

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