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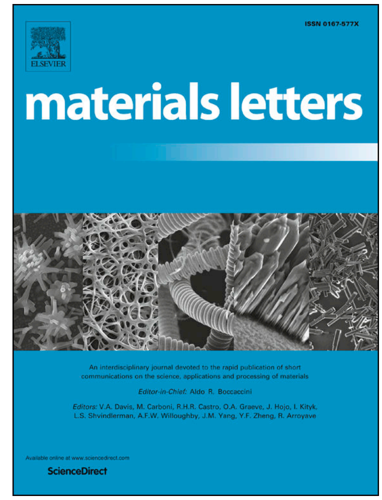

Dicyandiamide-Formaldehyde and Borassus Flabellifer Inflorescence Assisted Preparation of Low Surface Area Nitrogen-Doped Carbon as High-Performance Anode for Lithium-Ion Batteries

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Dicyandiamide-Formaldehyde and Borassus Flabellifer Inflorescence Assisted Preparation of Low Surface Area Nitrogen-Doped Carbon as High-Performance Anode for Lithium-Ion Batteries

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Abstract:

The heteroatom-doped disordered and nanostructured carbon materials have gained significant attention due to their enormous potential to improve the performance of energy applications. In this context, we have successfully developed a sustainable green synthesis of disordered and nanostructured nitrogen-doped carbon using pre-carbonized Borassus Flabellifer Male Inflorescence biomass coated with Dicyandiamide and Formaldehyde polymer, which subsequently subjected to thermal activation at 1000 ^{o}C for 6 hrs in nitrogen environment and it has lower surface area (30.76 m^2g^{-1}). The prepared N-doped carbon, when used as an anode in Li-ion batteries, delivered an outstanding reversible specific capacity of 655.8 mAh g^{-1} at a current density of 100 mA g^{-1} with the stable cycling behaviour for 1500 cycles. Even at a higher current rate (1000 mA g^{-1}), the prepared carbon displayed a reversible capacity of 351.9 mAh g^{-1}, thus making it a promising anode candidate for the next generation of high power lithium-ion batteries (LIBs).

Keywords: Nitrogen-doped carbon, Lithium-ion battery, Borassus Flabellifer, Disordered and Nanostructured carbon, Biomass

Introduction

Carbon materials in numerous structural forms are increasingly being investigated for physical and chemical properties such as high-temperature effective resistance, heat transfer, electrical conduction, and electrochemistry, which result in their widespread use in new types of energy storage devices [1, 2]. Many Researchers performed comprehensive studies on different carbon functional materials, contributing to a continuous improvement of the role of carbon materials [3, 4]. Nitrogen atoms are in the periodical table next to carbon atoms and are ideal for the substitution of carbon atoms in carbon products. The addition of heteroatom will alter the structure and distribution of the electron charge carriers on the surface by destroying carbon neutrality [5, 6]. The dicyandiamide-formaldehyde polymer (DFP) known as a type of organic flocculent polymer and it has several amino and hydroxyl groups that can activate the carbon but which can also be generated by adding a modification agent, to create new functions [7, 8] Biomass resources are most abundant and ecologically sustainable, high-carbon content and renewables.[9]. The Borassus Flabellifer inflorescence (BFI) originates in the warmer parts of India and is one of the most abundant biomass content in the worldwide due to the existence of numerous polyaromatic groups and suitable as electrode material for energy storage divisions. [10] In the present study, the nitrogen-doping disordered and hierarchical nanostructured carbon materials were prepared by thermal activation of pre-carbonized BFI biomass essentially modified with DFP. The synthesized nitrogen-doped carbon showed excellent electrochemical performances with outstanding cycling stability when employed as an anode in LIBs.

Experimental section

The designed molar ratio of Dicyandiamide, Formaldehyde, and the presence of ammonium chloride (1:3:0.5) was treated at 180 ^{o}C for 24 hrs in a hot air oven. The resulting polymer resin products were naturally cooled down to ambient temperature, washed with ethanol, and then vacuumed, at 90 °C, overnights. The condensation reaction between dicyandiamide and formaldehyde, according to shown in **Figure 1** reaction to form Dicyandiamide-formaldehyde polymer resin. The Borassus Flabellifer male inflorescence (BFI) biomass sample was annealed at 300 °C /2 hrs in a muffle furnace and finely the fine powered BFI carbon sample was processed [11]. The Dicyandiamide-formaldehyde assisted synthesis water-soluble polymer resin was combined with BFI Carbon material at a weight ratio of 1:2 and pyrolysis at 1000 °C /6 hrs at N_2 condition. The final sample was numerous times washed with ethanol and deionized water before drying at 60 °C /10 hrs. The prepared carbon material with Dicyandiamide-formaldehyde polymer and Borassus Flabellifer inflorescence is referred to as DFNCM.

The electrochemical performance of prepared Nitrogen-doped carbon anode materials (DFNCM) was evaluated using coin-type cells. For electrode preparation, the active material was coated by 80%, 10% PVDF, and 10% conductive carbon on Cu film using the NMP as a solvent and dried for 120 °C /12 hrs. Lithium metal act as a counter electrode, Commercial polypropylene as separator (TOB, China), and the electrolyte (1 M LiPF6 in a mixture of EC and DEC solvents, is 1:1 by volume) were fabricated into CR-2032 coin cells in the Ar-Atmosphere glove box (H2O and O2 in < 0.01 ppm; LAP-2000, china). The CV & EIS were achieved on a biologic workstation at 0.01–3 V (vs. Li+/Li).

Results and discussion

The morphology and structural features of the novel synthesized nitrogen-doped carbon was investigated using FESEM (Quattro FESEM, Thermo Fischer) and HRTEM (FEI-Tecnai G2 20 Twin HRTEM) respectively. Figure 1(a) showed the FESEM image of DFNCM which depicts the formation of broken wafer-like ordered carbon features as well as disordered crumbled carbon sheets. High-resolution TEM image results corroborate the existence of disordered arrays of graphitic lattice planes (**Figure 1 (b)).**

Figure 1(c) displays the XRD patterns (Rigaku, Bruker) of prepared DFNCM. Two broad peaks at ~25.9 and ~44 degree are attributed to the (002) and (100) crystal planes of sp2 hybridized carbon. The interlayer distance (d002- 0.362 nm), Lc (0.58 nm), and La (1.27 nm) parameters for the prepared DFNCM were shown in **Table 1.** These findings suggest that the prepared DFNCM has turbostratic disorder nature following the TEM result.

Figure 1(d) displays the DFNCM Raman spectrum (Alpha 300 R, WI Tec GmbH). In general, Raman spectra of every carbon sample contain two main peaks termed as D and G bands. The D-band (~1330 cm-1) of disorder or defects in the carbon whereas the G-band (~1585 cm^{-1}) of graphitized sp2 carbon are presented in this sample. The 2D band with an appearance of ~2850 cm^{-1} demonstrated also crystalline order of N-doped carbon graphic form. According to the biomass-derived carbon (DFNCM), it also displays to 2433 cm^{-1} that corresponds to D+D". The I_D/I_G and I_{2D}/I_G values are 0.88 and 0.19, respectively, denoting that introduce the nitrogen doping enhances the disorder degree of the carbon structure.

Figure 2(a) revealed a nitrogen adsorption and desorption isotherms (BETSORP max, microtracbel) of synthesized N-doped carbon. The DFNCM displays a typical type II isotherm that specifies the origin of these microspores. The surface area (BET; 30.76 m^2 g^{-1}), pore volume (VP; 0.186 cm^3 g^{-1}), and pore diameter (DP; 4.67 nm) were determined by absorption–desorption isotherms, and the results are shown in **Table 1.** The highly specific region and large pores of DFNCM is good promise with their porous structure **(Figure 2(b)).**

The XPS (Nexsa, Thermo Fisher) was examining the surface chemical composition of DFNCM. From Figure 2 (c), the survey spectra can be shown that the three major peaks of 285.0 eV (C1s), 532.0 eV (O1s) and 401.0 eV (N1s) binding energies in DFNCM. The De-convoluted N1s spectra (**Figure 2 (e)** display three peaks at 398.5 eV , 400.2 eV and 403 eV that are ascribed to pyridinic, pyrolitic and nitrogen atoms bonded to –C=O from these functionalities the formation of N-doped carbon has been confirmed.

To study the electrochemical performance of nitrogen-doped disordered and hierarchical nanostructured carbon materials (DFNCM) in LIBs, cyclic voltammetry (CV), experiments were performed by fabricating coin cells by metallic lithium as reference/counter electrode. **Figure 3(a)** displays the CV curves of the DFNCM electrode during the first five cycles and the 10th cycle. In the first discharge, two cathodic peaks at nearby ~1.0 V and 0.5 V can be detected, which are disappeared in subsequent cycles, consistent with the creation of solid electrolyte interface (SEI) film. Consequently, a broad redox peak at ~0.03 V can be observed, which can be attributed to Li+ de-intercalation from the DFNCM electrode. After the initial cycle that indicates the unresolved reversible cycling constancy, the CV data are overlapped.

As shown in **Figure 3 (b),** the DFNCM electrode exhibitions a first galvanostatic discharge/charge (NEWARE) reversible capacity of 1035/658.2 mAh g^{-1} and coulombic efficiency of 63.6% considerable greater than graphite. The irreversible capacity loss in the first discharge/charge process could be attributed to the development of the SEI layer. Moreover, long-standing cycling performance of DFNCM was tested at 100 mA g^{-1} delivered an outstanding reversible specific capacity of 655.8 mAh g^{-1}, and revealed a reversible capacity of 351.9 mAh g^{-1} at a higher current rate 1000 mA g^{-1} (**Figure 3 (c)).** The prepared DFNCM anode high capacity with stable cycling behaviour for 1500 cycles at 100 mA g^{-1} and the outcome is displayed in **Figure 3(d).** It could be concluded that the DFNCM with disordered and nanostructured nitrogen-doped carbon materials is promising anode materials of electrolyte and present additional active sites for Li storage.

Figure 3 (e) exhibits the electrochemical impedance spectroscopy (EIS) analysis at 1st, 500th, and 1000th cycles of DFNCM electrodes for LIBs in a frequency range of 0.01 Hz to 100 kHz. The semicircle diameters decreased with increasing the cycle number, representing a reduction in Rf and Rct resistances and revealing the rise in the electrical conductivity of the electrodes. The prepared DFNCM electrode confirmed high electronic conductivity and fast conversation among the Li+ and anode materials, which are the key factors for excellent battery performance.

Conclusion

In summary, an efficient method in preparing the disordered and hierarchical nanostructured Nitrogen-doped carbon material from Dicyandiamide-formaldehyde polymer and Borassus Flabellifer inflorescence carbon via a simple- step pyrolysis process has been reported for the first time. Promoting from the nitrogen-doped carbon electrode can offer more Li+ storage energetic sites and offer quick Li+ ions transmission stations. DFNCM electrode can reveal a high reversible capacity of 655.8 mAh g^{-1} at 100 mA g^{-1}. When the current density rises to 1,000 mA g^{-1}, an extraordinary reversible capacity of 351.9 mAh g^{-1} was also can be achieved. Therefore, the DFNCM electrode should be measured as a favorable anode electrode for LIBs as its excellent rate capability and outstanding cycling performance.

Acknowledgments

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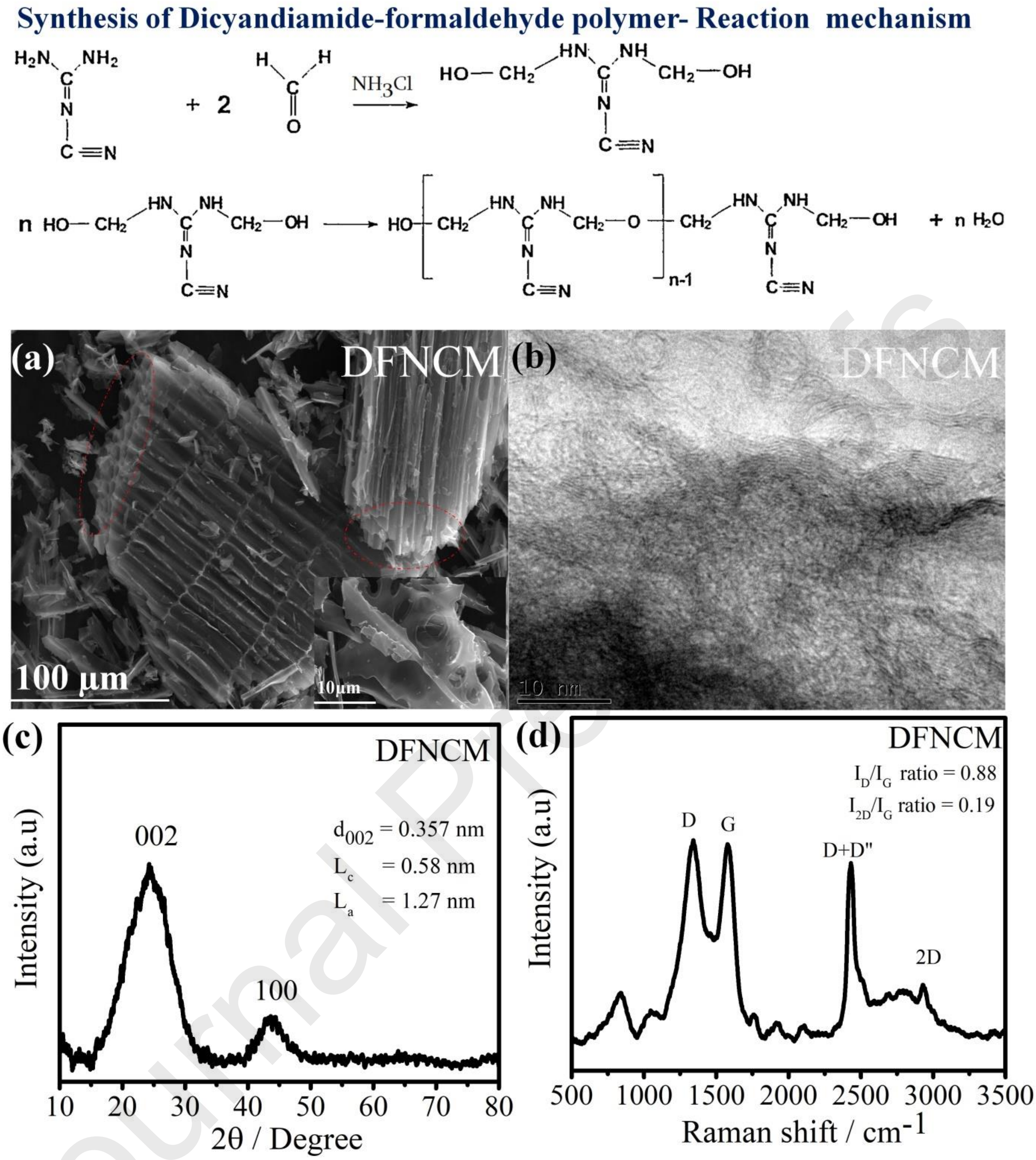


Figure 1 (a) FESEM, (b) HRTEM (c) XRD paten and (d) Raman spectrum of DFNCM and included Synthesis of Dicyandiamide-formaldehyde polymer- Reaction mechanism

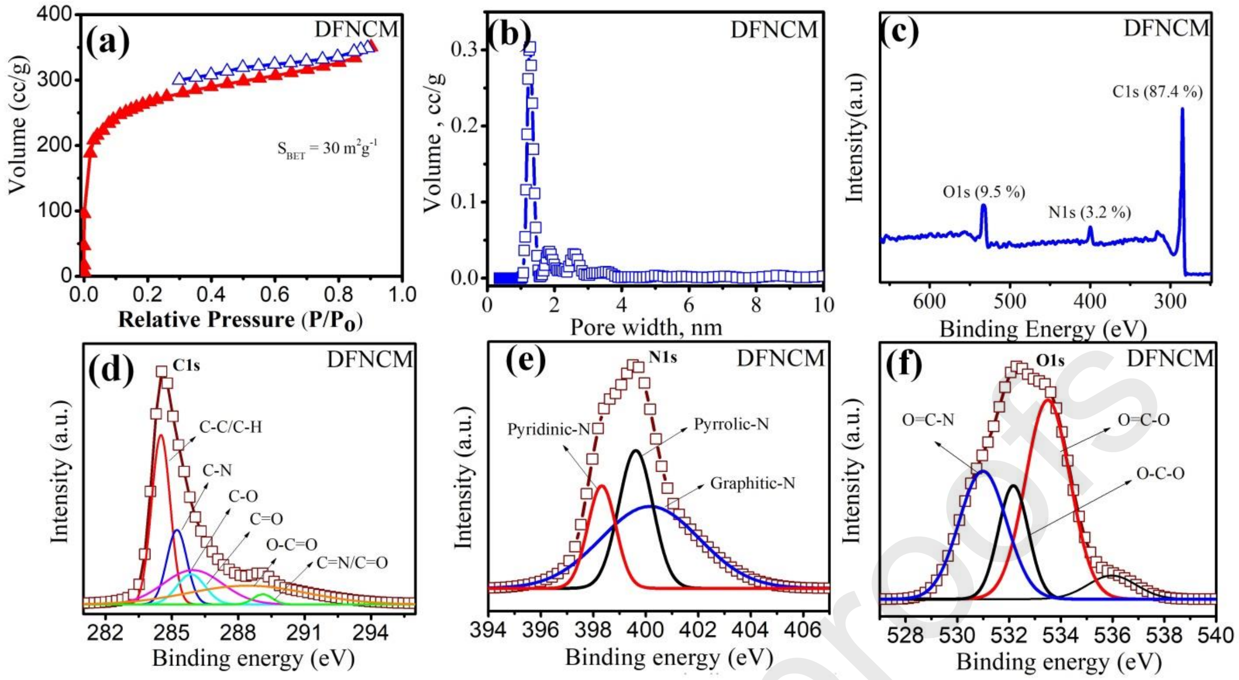


Figure 2 (a) BET (b) PSD and (c-f) XPS studies (C1s, N1s, O1s) of DFNCM

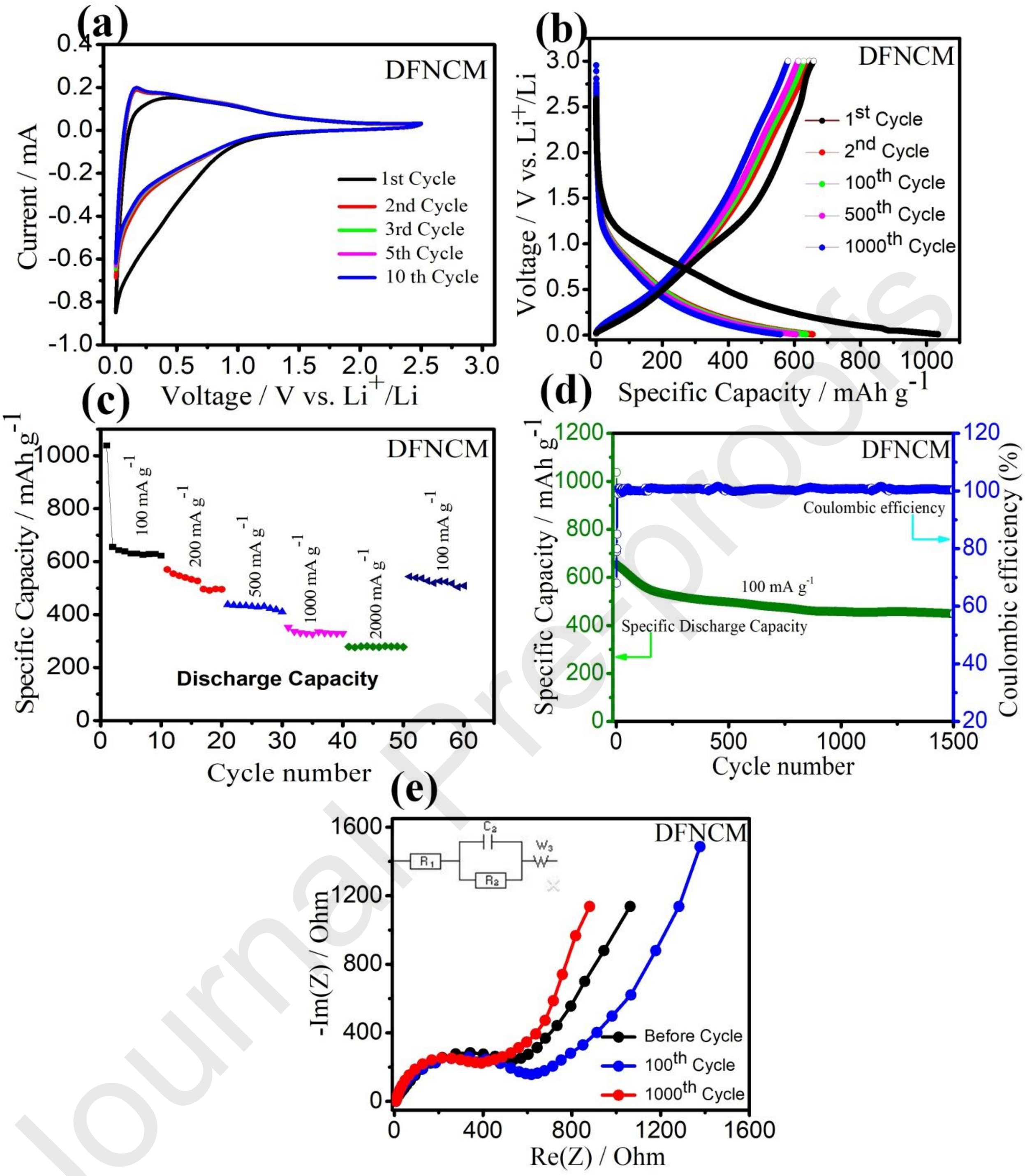


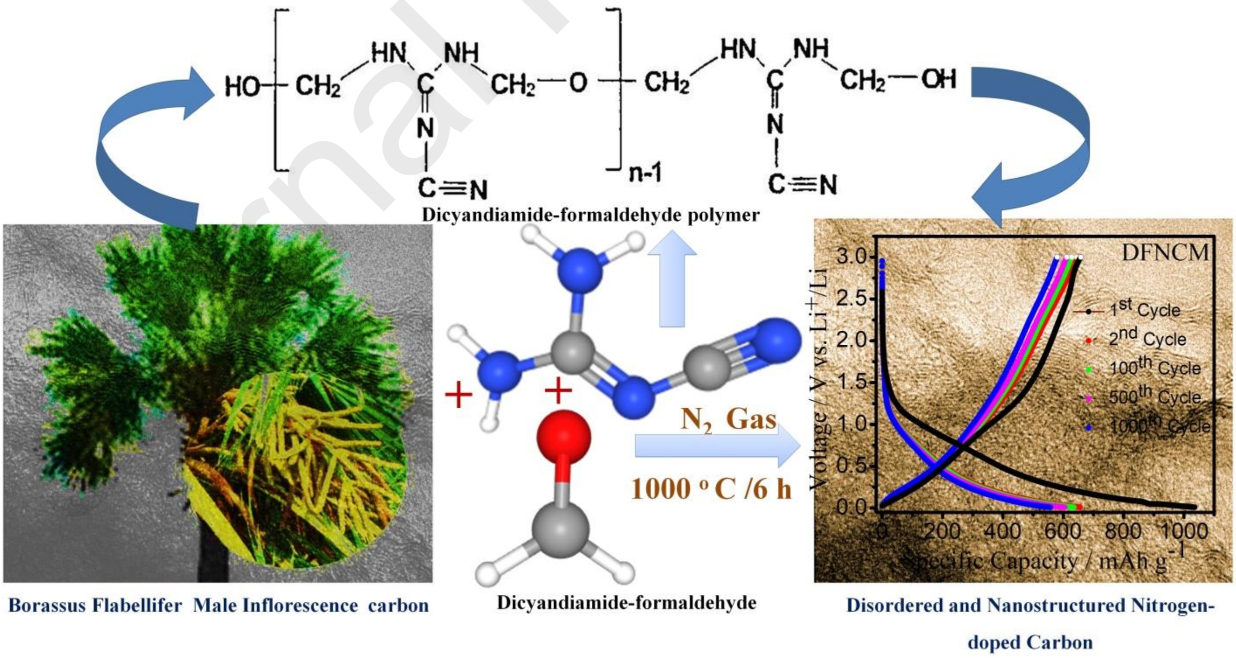
Figure 3 (a) Cyclic voltammetry studies, (b) GCD studies at different cycles, (c) GCD at different current density, (d) Cycling studies at 100mA g^{-1}, (e) EIS at before and after cycles.

Sample	I_D/I_G ratio	I_{2D}/I_G ratio	d_{002} (nm)	(L_c) (nm)	(L_a) (nm)	S_{BET}), ($m^2 g^{-1}$)	(V_P), ($cm^3 g^{-1}$)	(D_P), (nm)
DFNCM	0.88	0.19	0.362	0.58	1.27	30.76	0.186	4.67

L_c - Crystalline Height; L_a -Crystalline Width; S_{BET} - BET surface area; V_P - Pore volumes; D_P-Mean pore diameter.

Table 1 Basic morphology result of prepared nitrogen-doped carbon material (DFNCM)

Graphical abstract



Schematic illustration of Dicyandiamide-Formaldehyde Condensate Assisted Synthesis of disordered and hierarchically nanostructured nitrogen-doped carbon material.

Highlights

- N-doped carbon anode material from Borassus Flabellifer Inflorescence for LIBs.
- Activation and nitrogen source used as Dicyandiamide and Formaldehyde polymer.
- An outstanding reversible specific capacity of 655.8 mAh g-1 at 100 mA g-1
- The excellent reversible capacity of 352 mAh g-1 at higher current rate 1000 mA g-1