A high-capacity dual-ion full battery based on nitrogen-doped carbon nanosphere anode and concentrated electrolyte

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Abstract

Dual-ion batteries (DIBs) are often criticized for their low discharge capacity and poor cyclic capability despite their inherent high working voltage, low manufacturing cost and environmental friendliness. To solve these shortcomings, many attempts and efforts have been devoted, but all ended in unsatisfactory results. Herein, a hierarchical porous carbon nanosphere anode with high nitrogen doping is developed, which exhibits fast ion transport kinetics and excellent Li\(^+\) storage capability. Moreover, employing concentrated electrolyte is expected to bring a series of advantages such as stable SEI for facilitating ion transmission, enhanced cycling performance, high specific capacity and operation voltage. These advantages endow the assembled full DIBs with excellent performance as a super-high specific discharge capacity of 351 mAh g\(^{-1}\) and can be cycled stably for 1300 cycles with Coulombic efficiency (CE) remaining at 99.5%; a high operating voltage range of 4.95–3.63 V and low self-discharge rate of 2.46% h\(^{-1}\) with stable fast charging-slow discharging performance. Through electrochemical measurements and physical characterizations, the possible working mechanism of the proof-of-concept full battery and the structural variations of electrodes during cycling are investigated. The novel battery system design strategy in this work will promote the development of high-performance DIBs.

1 Introduction

The soaring demand for sustainable electrochemical energy storage from intermittent renewable sources such as solar, wind, and tidal energy has triggered the urgent pursuit of cost-effective electrochemical energy storage equipment [1–3]. Although lithium-ion batteries (LIBs) still have the largest market share and are widely used in mobile phones, laptops and electric vehicles, they suffer from low output voltage and high costs [4–6]. On the contrary, DIBs can adopt graphite as both anode and cathode, and its unique anion intercalation mechanism endows a high working voltage and energy density, which make up for the shortcomings of LiBs [7–10]. However, it is difficult to realize the practical application of DIBs. A key point to be illustrated is the great demand for anodes since graphite anodes exhibit scanty sites for Li\(^+\) storage and poor cycle performance [11–13]. Compared with graphitized carbon, amorphous carbon doped with heterogeneous elements formed by high-temperature pyrolysis generally display some unexpected properties: (1) Defects generated during pyrolysis can be regarded as active sites to store Li\(^+\) [14–17]; (2) Emerging greater layer spacing, which achieves rapid transmission of Li\(^+\) and a high (de)lithiation rate [18–20]; (3) Doped heterogeneous elements help to improve structural stability and ionic conductivity with additional Li\(^+\) storage sites [21–23].

Nitrogen doping of amorphous carbon is a representative strategy to fulfill high capacity, long life and an excellent rate carbonaceous anode [24–28]. Currently, template-assisted pyrolysis is usually used to synthesize nitrogen-doped carbon (NDC) anodes [29–32]. For instance, Yang et al. used zinc oxide nanospheres and polyacrylonitrile as the hard template and precursor to prepare an un-pyrolyzed electrospun membrane by the electrospinning method, and then obtain the necklace-like porous NDCs (NHC\(_2\)-NH\(_3\)/Ar) by pyrolyzing in NH\(_3\) and Ar atmospheres sequentially [30]. The stable cycling proficiency
of the NHC$_2$-NH$_3$/Ar electrode is demonstrated by showing a reversible capacity of 161.3 mAh g$^{-1}$ after more than 1600 cycles at 1000 mA g$^{-1}$. Ge et al. uniformly mixed g-C$_3$N$_4$ with zinc powder, followed by two-step pyrolysis at 500 °C and 800 °C in argon [31]. Finally, the metal ions were removed with acid to obtain an NDC microsphere with hierarchical structure (CMSs). The assembled full battery based on CMSs anode delivers a retention rate of 78% for 1900 cycles at 500 mA g$^{-1}$. Xiong et al. synthesized a nitrogen/oxygen dual-doped carbon (NOHPHC) by pyrolyzing and etching a type of metal-organic framework based on a self-template method [32]. Therefore, the NOHPHC electrode exhibits a capacity of 123 mAh g$^{-1}$ after 1100 cycles with a retention rate of 69.5%.

However, the above synthesis strategies based on the template method are cumbersome and complicated, and difficult to guarantee the purity. An ideal tactic is to prepare the NDC anode with hierarchical porous structure through one-step direct pyrolysis of the homologous precursor [33–36]. Zhang et al. prepared accordion-shaped NDC by directly pyrolyzing uric acid powder at 900 °C, the special layered carbon structure can suppress volume expansion to improve stability [33]. Qiu et al. directly pyrolyzed g-C$_3$N$_4$ at 700 °C to obtain layered NDC, which has excellent Li$^+$ storage capability with a fast rate [34]. Alshareef et al. obtained 3D-NDC by directly pyrolyzing PMA-MA supramolecules at 750 °C, which were composed of carbon nanosheets and disordered crystal structure with ultra-high edge-nitrogen-doping of 16.8 at% [35]. The full battery with the 3D-NDC electrode can release a high capacity of 241 mAh g$^{-1}$ after 100 cycles with a low self-discharge rate of 0.088% per hour.

A crucial point in the exploitation of high-performance dual-carbon lithium-based full batteries is the demand for an appropriate electrolyte system, since electrolyte is the single source of active ions required to maintain a sufficiently high concentration [37–38]. Conventional low concentration (< 1 M, 1 M = 1 mol/L) electrolytes based on ethylene carbonate usually exhibit sub-optimal performance: poor cyclic stability due to the continuous decomposition of electrolyte under the high voltage and fragile SEI [39]; low discharge capacity because of the co-intercalation of EC molecules [40, 41]. Interestingly, concentrated electrolytes usually display outstanding performances: the formed sturdy SEI is conducive to the (de)intercalation of active ions [42]; reduce the potential of the anion intercalated into graphite cathode and improve the reduction stability [43]; provide enough active ions, which is expected to deliver a high discharge capacity [44]. In addition, ionic liquids (ILs) are ideal candidate solvents because of their wide electrochemical window, non-flammability, and avoidance of solvent molecular co-intercalation [45–47]. Nevertheless, considering the high viscosity and low solubility of ILs, it is a satisfactory choice to combine the respective superiorities of organic solvents and ILs for exploiting a novel organic solvent-ILs mixed electrolyte, which is promised to bring unexpected electrochemical performance.

Herein, an innovative immediate pyrolysis strategy is shared for the preparation of 3D-NDC nanosphere anode (3D-NDCS) with a layered porous structure. Matched with concentrated organic-IL mixed electrolyte (4 M EMC-Pyr$_{14}$TFSI-5%ES) and natural graphite (NG) cathode, the assembled full battery (NDCS//NG-DIB) exhibits high discharge specific capacity, excellent rate capability and stable cyclic performance. Moreover, through a series of physical and electrochemical characterizations, the Li$^+$
storage mechanism of 3D-NDCS and the structural variations in different charging-discharging stages are investigated, and some opinions on whether the DIB of this system can be realized in practical applications are put forward.

2 Experimental Section

2.1 Chemical Preparation

Nitrogen-doped carbon (NDC) was synthesized by direct pyrolysis of melamine foam. First, melamine foam was placed in a corundum crucible with a lid, then the crucible was put into a tube furnace filled with argon, and the temperature is programmed to 1000 °C for 2 hours with a heating rate of 5 °C/min. After cooling, the sample was fully ground uniformly, and the obtained powder is directly used as the anode without further purification.

2.2 Physicochemical characterization

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) images were taken on a scanning electron microscopy (Berlin, ZEISS, Germany). The SEM and EDS of the NDC sample was tested using an aluminum plate as a substrate. X-Ray Diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with a Cu Kα radiation (λ = 1.5406 Å). Power XRD was recorded in the 2 theta (5°-90°, 10°/min) with a Cu-Kα radiation (40 kV, 40 mA). Raman spectra were collected on a LabRAM ARAMIS micro-Raman spectrometer (Horiba-Jobin Yvon, Germany) using a cobalt laser (473 nm) with a 1% filter. Fourier-transform infrared spectra (FTIR) was collected on a Nicolet iS10 FTIR spectrometer (ThermoFisher Scientific, USA). X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos Axis Supra photoelectron spectrometer (Shimadzu, Japan). The specific surface areas and pore size distributions were evaluated by N₂ adsorption isotherms tested by an ASAP 2420 adsorption/desorption analyzer (Micrometrics, USA).

2.3 Electrode preparation and electrochemical tests

The Natural graphite cathode was prepared by adding natural graphite powder (3000 mesh), AB, and PVDF into a weighing bottle containing N-methyl-pyrrolidone (NMP) solvent (90:2:8, w/w/w), stirring overnight until uniformly mixed. Then the prepared slurry was poured onto the aluminum foil, and the film was then coated evenly with a film applicator to a thickness of 200 µm. Finally, it was placed into a vacuum drying oven to dry overnight at 100°C. Similarly, the NDC anode was prepared like the natural graphite cathode with the mass ratio of 7:2:1, and the thickness was 100 µm. Both of the natural graphite cathode and NDC anode were cut into wafers (diameter: 14 mm). In addition, the active materials loading of anode and cathode were ~ 1.0 and 2.0 mg/cm², respectively.

For the test of DIB anode, 4.0 mol/L LiTFSI in Ethyl Methyl Carbonate: N-butyl-N-methylpyrrolidinium bis(trifluoromethyl sulfonyl)imide (1:1, v:v) with addition of 5% Vinyl sulfite was used as the electrolyte (abbreviated as 4 M LiTFSI-EMC-Pyr₁₄TFSI-5%ES). Batteries were assembled by using the CR2025 coin-
type cell composed of a natural graphite cathode, a NDC anode, one piece of glass fiber diaphragm and 110 µL electrolyte was added. Galvanostatic charge-discharge (GCD) test, rate performance test, self-discharge performance test, fast charging-slow discharging performance test were conducted on a CT-4008T-5V10mA-164 Neware battery tester (Neware, Shenzhen, China). The Cyclic voltammetry (CV) (0.1 mV s\(^{-1}\)) and Electrochemical impedance spectroscopy (EIS) measurements at 200 mA g\(^{-1}\) were conducted by electrochemical workstation (Gamry, US).

### 3 Results And Discussion

As shown in Scheme S1, melamine foam was used for the first time as a carbon precursor for the direct pyrolysis synthesis of 3D-NDCS. Different from powdered melamine, foamed melamine displays a porous network structure, which is conducive to the formation of 3D porous carbon skeleton during pyrolysis. Finally, the carbon skeleton gradually collapses and polymerizes when heated, forming a 3D porous sphere. In addition, the nitrogen content of melamine accounts for a high proportion of 66.7%, which is expected to bring high nitrogen doping. Figure S1 shows the scanning electron microscope (SEM) image of melamine foam after pyrolysis at 1000°C. The overall shape formed by the arrangement of rows of spheres, specifically, each column presents a candied haws-like string morphology composed of nano-sized porous spheres with a diameter of 40–60 nm, which helps to improve the transmission kinetics of active ions and ensure the adequate infiltration of electrolyte. The broad typical peak (002) with low peak intensity indicates the imperfect alignment of 3D-NDCS with large layer spacing (Fig. 1a), which is caused by the formation of amorphous structure due to the release of pyrolysis gas during the carbonization process of melamine foam [33, 34]. The R value reflecting the crystallinity of amorphous carbon introduced by Dahn is 3.36, indicating a low crystallinity with a high disorder of 3D-NDCS [48]. It can also be proved from the Raman spectrum that the G band at ~1580 cm\(^{-1}\) is quite weak, and the value of \(I_D/I_G\) is 1.01, shows the large amount of defects and high amorphous state of 3D-NDCS (Fig. 1b) [49]. The results of EDX mapping represent an ultra-high nitrogen doping content of 36.46% (Figs. 1c and S2), which is significantly higher than most reported nitrogen doping levels. It can be proved from the FT-IR analysis in Figure S3 that the broad absorption peak around 1130 cm\(^{-1}\) is attributed to the stretching vibration of C-N bond, and the absorption peaks near 1560 and 1655 cm\(^{-1}\) are associated with C = N and N-H bond [50, 51], respectively. Figure 1c suggests that C, N, and O elements are uniformly distributed. The relative ratios of pyridine nitrogen (N6), pyrrole nitrogen (N5), graphitized nitrogen (NQ), and nitrogen oxide (NO) obtained via fitting high-resolution N1s XPS spectra are 42.3%, 39.5%, 14.0% and 4.2%, respectively, with a high proportion of 81.8% for edge-nitrogen (N6 and N5), which is of great significance to improve the Li\(^+\) storage capacity of 3D-NDCS (Fig. 1d) [32, 34, 52]. Remarkably, the \(N_2\) adsorption/desorption curves show a hierarchical pore distribution of micropores, mesopores and macropores for 3D-NDCS, which helps to store more active ions (Fig. 1e). Besides, the low BET specific surface area of 16.731 m\(^2\)/g is expected to ensure sufficient contact with the electrolyte and inhibit the occurrence of parasitic reactions (Fig. 1f), thus forming a steady SEI film [53, 54].
The Li$^+$ storage capability and electrochemical performances of the 3D-NDCS electrode was investigated by cyclic voltammetry scanned between 2.5-5.0 V. Fig. 2a shows the CV curves at a scan rate of 0.3 mV/s. The reduction peaks near −2.8 and −3.2 V in the first circle can be attributed to the decomposition of electrolyte for the formation of SEI [55, 56]. Notably, they disappear in the subsequent cycles, indicating the stability of SEI. Two pairs of redox peaks near −4.8 and −4.2 V correspond to the electrochemical reaction process. Moreover, all the curves except the first cycle coincide, indicating that the storage of Li$^+$ is a stable and reversible process [49, 57]. The galvanostatic charge-discharge (GCD) curve of NDCS//NG-DIB at 1 C (1 C = 100 mA g$^{-1}$) displays typical active ion (de)intercalation characteristics with two pairs of charge/discharge plateaus (Fig. 2b), matching with the redox peaks in CV curves (Fig. 2a). Figure 2c exhibits the corresponding dQ/dV differential profile that each peak is consistent with the platform in the GCD curve. The charging process can be identified as three regions of 3.63–4.39 V (stage I), 4.39–4.83 V (stage II), and 4.83–5.0 V (stage III), representing different stages of Li$^+$ intercalation into 3D-NDCS [58–60]. Similarly, the discharge process is also divided into three periods of 4.95–4.66 V, 4.66–4.27 V, and 4.27–3.63 V, implying different stages of Li$^+$ deintercalation from 3D-NDCS. Furthermore, the NDCS//NG-DIB displays an operating voltage range of 4.95–3.63 V with a medium discharge voltage ($V_m$) of 4.28 V, which is much higher than commercial LiBs. To explore the Li$^+$ storage behaviour and kinetics of the 3D-NDCS electrode, CV curves based on different scan rates have been obtained (Fig. 2d). Specifically, these curves present a rectangular-like shape with clear redox peaks, indicating the synergistic effect of diffusion and capacitive behaviour [61]. This synergistic effect can be quantitatively analyzed based on the power-law relationship between $i$ (peak current) and $v$ (scan rate): $i = a v^b$, where the value of $b$ between 0.5-1 can be determined by plotting log($i$) vs log($v$), the $b$-value close to 0.5 or 1 meaning a diffusion-controlled or capacitive-controlled process, respectively [62, 63]. Figure 2e shows the $b$-values of the anodic and cathodic peaks are calculated to be 0.8226 and 0.8108, respectively, indicating that the kinetics of 3D-NDCS is mainly attributed to the capacitive-controlled process. Quantitatively, the mixed mechanisms can be divided into two separate mechanisms at a fixed potential by $i(V) = k_1 v + k_2 v^{1/2}$, where $k_1$ and $k_2$ are constants, and $k_1 v$ and $k_2 v^{1/2}$ represent capacitance contribution and diffusion contribution, respectively [64]. As shown in Fig. 2f, correspondingly, the capacitance contribution to Li$^+$ storage at 0.1 mV/s is 0.738. In addition, it increases to 0.829, 0.863 and 0.882 as the scan rates increase to 0.3, 0.5, and 0.7 mV/s, respectively.

To further investigate the rate capability and cyclic performance of NDCS//NG-DIB, a proof-of-concept full battery based on a 4 M concentrated electrolyte and a 3D-NDCS anode is constructed. Figure 3a demonstrates the typical GCD curves at different current densities from 1 to 15 C with voltage range of 2.5-5.0 V. As the current density increases, a slight charge-discharge plateau separation is observed, indicating the occurrence of electrochemical polarization. It can be proved from the dQ/dV differential curves in Figure S4 that as the rate increases, the oxidation/reduction peaks shift to a high/low potential with the peak intensities decreasing [49, 65]. Nevertheless, the separation is slow with the voltage platforms corresponding to the (de)intercalation of active ions still being clearly examined, indicating the weak polarization and fast kinetics behaviour. Moreover, specific discharge capacities (SDC) of 335, 278,
242, 223, 185, and 156 mAh g\(^{-1}\) can be delivered at the rate scope of 1, 2, 3, 5, 10, and 15 C (Fig. 3b), the SDC can be restored to its initial value and cycled stably when the rate returns to 2 C, demonstrating the excellent reversibility and rate capability of NDCS//NG-DIB. For comparison, we also assembled a full DIB based on diluted electrolyte of 1 M, which displays unsatisfactory performance compared to concentrated electrolyte. As well as the increase of current density, the polarization becomes more serious and the charge/discharge plateaus tilt (Figure S5). Only 163, 142, 119, 88, 63, and 49 mAh g\(^{-1}\) achieved at 1, 2, 3, 5, 10, and 15 C, respectively (Figure S6). Figure 3c shows the cycling performance of NDCS//NG-DIB based on concentrated/diluted electrolyte at 1 C. On the one hand, the initial specific discharge capacity (ISDC) based on concentrated electrolyte is as high as 351 mAh g\(^{-1}\), and the capacity retention rate (CRR) of 95% after 80 cycles. Furthermore, the GCD curves of various cycles basically overlap (Fig. 3d), indicating outstanding cyclic stability, which showcases the best performance of DIBs reported so far. On the other hand, a ISDC of 148 mAh g\(^{-1}\) based on diluted electrolyte is released, then decreases continuously in subsequent cycles with a limited SDC of 66 mAh g\(^{-1}\) obtained after 80 cycles. The GCD curves display poor cyclic stability and serious polarization with disappearing charge/discharge plateaus as shown in Figure S7. The enormous discrepancy mainly benefits from the formation of sturdy SEI via the use of concentrated electrolyte. Researches by Atsuo Yamada et al. have shown that concentrated electrolytes are not only beneficial to the rapid transport of Li\(^+\) and steady circulation, but also inhibit the further decomposition of electrolyte and occurrence of side reactions, resulting in better electrochemical performance [42, 43, 66, 67]. This can be inferred from the Nyquist plots based on electrochemical impedance spectroscopy (EIS) in Fig. 3e and Figure S8, the intermediate frequency semi-circle represents the charge transfer resistance (R\(\text{ct}\)) at the electrode/electrolyte interface. The initial R\(\text{ct}\) based on concentrated electrolyte is slightly larger than that of diluted electrolyte, which is owing to the higher viscosity of high-concentration electrolyte. Interestingly, the R\(\text{ct}\) of diluted electrolyte is significantly higher than that of concentrated electrolyte in subsequent cycles. It is caused by the utilization of diluted electrolyte resulting in a fragile SEI, which will lead to the continuous decomposition of electrolyte and the formation of SEI. Besides, the NDCS//NG-DIB based on concentrated electrolyte exhibits a quite stable \(V_m\) up to 4.2 V during the long-cycling process (Fig. 3f). As the rate up to 4 C, the ISDC based on concentrated electrolyte is 255 mAh g\(^{-1}\) with no capacity fade after 200 cycles, while the ISDC based on diluted electrolyte is only 110 mAh g\(^{-1}\) with a CRR of 71% (Figure S9). Surprisingly, the battery still shows superior electrochemical performance even at a high rate of 15 C. The ISDC is 166 mAh g\(^{-1}\), and it can be continuously cycled for 1300 cycles without capacity degradation with the CE maintains at ~ 99.5%. While the ISDC of 46 mAh g\(^{-1}\) based on diluted electrolyte is much less than that of concentrated electrolyte and decays continuously to 36 mAh g\(^{-1}\) after 1300 cycles, signifying a poor cycling performance.

Severe self-discharge will limit further practical application, especially in dual-graphite or dual-carbon systems, where the batteries usually deliver a serious self-discharge rate [68–70]. Therefore, the self-discharge performance was conducted. First, charging the full battery to the upper cut-off voltage of 5.0 V, and then discharging it after resting for 24 h. Figures 4a-b show the voltage-time curves of (un)resting,
the battery still maintains a voltage of 4.41 V after resting. Consequently, the self-discharge rate of the system is calculated as 2.46% h⁻¹, which is considerably lower than that of the reported DIBs. In addition, stable fast charging and slow discharging can not only shorten the charging time, but also increase the usage time of batteries. Therefore, the performance was tested by fast charging at an ultra-high rate of 20 C, then slowly discharged at a low rate of 1 C to investigate the cyclic stability. The first 10 cycles of fast charging-slow discharging shows that the battery is fully charged within 5 minutes, while the discharging time exceeds 100 minutes (Fig. 4c). Besides, the ISDC reaches 176 mAh g⁻¹ and steadily increases to 186 mAh g⁻¹ after 300 cycles (Fig. 4d). This results in excellent fast charging-slow discharging performance, indicating that this dual-ion full battery system shows excellent stability with great potential for further practical application.

To elucidate the working mechanism of NDCS//NG-DIB. X-ray photo-electron derivative spectroscopy (XPS) was performed to characterize and analyze the elements of electrodes during the GCD processes, and the corresponding results are presented in Fig. 5. Figure 5a shows the high-resolution Li 1s spectrum. A sharp Li 1s characteristic peak appears at the fully charged stage, indicating the intercalation of Li⁺ [55]. After being fully discharged, the characteristic peak disappears completely, which means the reversible (de)intercalation of Li⁺. Moreover, a distinct F 1s characteristic peak appears after being fully charged (Fig. 5b). According to the previous work, which is due to the sharp decrease of free solvent molecules in the concentrated electrolyte, the anion (TFSI⁻) preferentially decomposed to form a robust SEI [42, 43, 66, 67, 71–73]. As shown in the high-resolution C 1s spectrum (Fig. 5c), the C-N characteristic peak significantly strengthened [52, 74]. Besides, a new characteristic peak corresponding to the decomposition of TFSI⁻ appears [75]. After being fully discharged, the characteristic peaks of F 1s and C-N remains basically unchanged, while the decomposition peak of TFSI⁻ weakened, indicating the formation of a robust SEI that no longer consumed electrolyte. As for NG cathode, the high-resolution S 2p spectra appears after being fully charged because of the intercalation of TFSI⁻ (Fig. 5d), which becomes weaker with the deintercalation of TFSI⁻ after being fully discharged. Furthermore, the (de)intercalation of TFSI⁻ at NG cathode can be demonstrated from the FT-IR spectra based on pristine and fully charged/discharged stages. As shown in Fig. 5e, stretching vibration peaks corresponding to C=S, S=O, C-F and N-H appears at ~1047, 1127, 1188 and 1324 cm⁻¹, respectively after being fully charged, implying the intercalation of TFSI⁻ [61, 65, 76]. Then all the characteristic peaks are significantly weakened due to the deintercalation of TFSI⁻ after being fully discharged. Combined with the XRD results (explained in the following section), the remaining signal peaks are mainly due to the residual electrolyte and the decomposition of TFSI⁻ and ES to form a CEI on the surface of cathode, just as there are still strong N-S (Figure S10), Li-F (Figure S11) and TFSI⁻ decomposition peaks (Figure S12) after being fully discharged.

Combined with the above analysis, the working mechanism of the full battery is shown in Fig. 6, and the electrode reactions involved are as follows:
Anode: \( xC_A + Li^+ + e^- \leftrightarrow C_Ax(Li) \) where A represents Anode

Cathode: \( yC_C + TFSI^- \leftrightarrow C_Cy(TFSI) + e^- \) where C represents Cathode

Overall: \( xC_A + Li^+ + yC_C + TFSI^- \leftrightarrow C_Cy(TFSI) + C_Ax(Li) \)

XRD and Raman characterizations were performed to further explore the (de)intercalation behaviour of \( Li^+/TFSI^- \) with the concentrated electrolyte at the selected charged/discharged states. Figure 7a shows the corresponding time-voltage curve of the full battery for XRD measurement. As for NG cathode, the intensity of 002 characteristic peak at 26.5° gradually decreases during the charging process (Fig. 7b), and a new characteristic peak is split after being fully charged, which is caused by the formation of graphite intercalation compounds (GICs), corresponding to a layer spacing of 3.9 Å with intercalation stage of 1 [77–79]. The split peak disappears during the subsequent discharging process, while the 002 peak recovers to its original intensity after being fully discharged. Moreover, it remains a comparable intensity to the pristine peak even after 200 cycles, indicating an outstanding reversibility of the (de)intercalation process with excellent structural stability of NG. The Raman spectra of cathode in Fig. 7e can also corroborate the reversible (de)intercalation of TFSI\(^-\). The D band and G band located at ~ 1360 cm\(^{-1}\) and ~ 1580 cm\(^{-1}\) represent the defects and sp\(^2\) carbon atomic plane vibrations of the graphitic layer, respectively, and the ratio of \( I_D/I_G \) is usually used to measure the disorder degree of graphite [49, 69, 73]. The \( I_D/I_G \) ratio gradually increases during the charging process, representing a reduction of the crystallinity due to the intercalation of TFSI\(^-\). During the following discharging process, the \( I_D/I_G \) ratio gradually decreases and the crystallinity of graphite recovers with the deintercalation of TFSI\(^-\). For 3D-NDCS anode, as shown in Fig. 7c, the 002 peak gradually decreases with the continuous intercalation of \( Li^+ \) during the charging process. In the meantime, the D band in the Raman spectrum continuously enhances, accompanied by an increase in the \( I_D/I_G \) ratio (Fig. 7f), indicating the enhancement of layer spacing and disorder of anode. During the discharging process, the 002 peak returns to original strength with the continuous deintercalation of \( Li^+ \), which is manifested in the decrease of D band and \( I_D/I_G \) ratio, and the crystal structure of anode gradually recovers. Remarkably, all characteristic peaks do not shift during the entire process, and still maintain the comparative intensity to pristine peak after 200 cycles, proving the excellent reversibility of (de)intercalation and splendid structural stability.

The structure and morphology evolution of electrodes after 200 cycles were investigated by scanning electron microscope (SEM). On one hand, Figures S13a-b show the SEM images of NG cathode after 200 cycles. The lamellar structure of graphite can be clearly seen without any volume expansion and structural exfoliation, which proves the structural stability of NG. On the other hand, the surface morphology and structure of anode after 200 cycles are shown in Figures S13c-d, the complete 3D spherical structure is still displayed, indicating the splendid cyclic stability, which is consistent with the conclusion of XRD and Raman in Fig. 7.
4 Conclusion

The high-nitrogen-doped hierarchical porous carbon nanosphere anode was synthesized by a one-step direct pyrolysis method, which shows fast ion transport kinetics and excellent Li\(^+\) storage performance. Besides, the adoption of concentrated electrolyte is conducive to the formation of stable SEI and improves the intercalation capacity with reversible transmission of active ions. The constructed full battery exhibits a series of excellent electrochemical performances: (1) A super-high ISDC of 351 mAh g\(^{-1}\) at 1 C with a CRR of 95% after 80 cycles; (2) The ISDC is 166 mAh g\(^{-1}\) at a high rate of 15 C and can be cycled stably for 1300 cycles with CE remains at 99.5%; (3) A high operating voltage range of 4.95–3.63 V and high median discharge voltage of 4.2 V; (4) Low self-discharge rate of 2.46% h\(^{-1}\) and stable fast charging (fully charged within 5 minutes) and slow discharging (up to 100 minutes during discharge). The working mechanism of NDCS//NG-DIB is explained by XPS and FT-IR, and the excellent structural stability of electrodes is demonstrated by XRD, Raman and SEM, which is one of the reported DIBs with best preponderance. It is expected to shed light on the development of high-performance and large-scale practical application in the future for DIBs.

Declarations

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

References


62. P. Lu, Y. Sun, H. F. Xiang, X. Liang, Y. Yu. 3D amorphous carbon with controlled porous and disordered structures as a high-rate anode material for sodium-ion batteries. Adv Energy Mater.


75. X. Li, X. W. Ou, Y. B. Tang. 6.0 V high-voltage and concentrated electrolyte toward high energy density K-based dual-graphite battery. Adv Energy Mater. 10(41), 2002567 (2020).


**Figures**

**Figure 1**

**Structural and compositional characterizations of the 3D-NDCS** (a) XRD. (b) C, N and O element content proportion. (c) EDX mapping of C, N and O elements. (d) High resolution XPS N1s spectrum. (e) Pore size distribution. (f) N\(_2\) adsorption/desorption curve.
Figure 2

**Electrochemical performance and kinetic analysis of 3D-NDCS anode** (a) CV curves of different cycles under 0.3 mV s\(^{-1}\). (b) Galvanostatic charge-discharge curve. (c) Corresponding dQ/dV differential profile. (d) CV curve at different scan rates. (e) Corresponding b value deriving from the relationship of i=av\(^b\). (f) Contribution fraction of the capacitive behaviour to the capacities at different scan rates.
Figure 3

Electrochemical measurements of the NDCS//NG-DIB based on concentrated/diluted electrolyte (a) Galvanostatic charge-discharge curves under different rates. (b) Rate capability performance. (c) The long-term cycling performance under 1 C. (d) GCD curves under different cycles at 3 C. (e) EIS curves and the corresponding equivalent circuit after different cycles. (f) Corresponding medium discharge voltage during the cycling test. (g) The long-term cycling performance under 15 C.
Self-discharge and fast charging-slow discharging performance test

Figure 4

Galvanostatic charge-discharge curves of (a) Unresting and (b) Resting for 24 h. (c) The first 10 cycles of charging at 20 C and discharging at 1 C and (d) Corresponding cycle performance for 300 cycles.
Figure 5

Investigations on the working mechanism based on 3D-NDCS and concentrated electrolyte. High-resolution characteristic peaks of Li 1s (a), F 1s (b) and C 1s (c) based on different charge-discharge states. (d) The FT-IR image at pristine, fully charged/discharged states.
Figure 6

The working mechanism of the proof-of-concept full battery
Figure 7

**XRD and Raman characterizations during charging and discharging** (a-c) XRD images and (d-f) Raman spectrums of NG cathode and 3D-NDCS anode based on the selected stages.

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