



High-power lithium-ion hybrid supercapacitor enabled by holey carbon nanolayers with targeted porosity

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HIGHLIGHTS

- Holey carbon nanolayer (HCN) with targeted porosity is fabricated.
- HCN is used as both cathode and anode of lithium-ion hybrid supercapacitor (LIHS).
- Unbalanced kinetics between cathode and anode in LIHS can be mitigated by HCN.
- HCN-based LIHS keeps 114 Wh kg⁻¹ at an ultra-high power density of 65 kW kg⁻¹.

ARTICLE INFO

Keywords:

Lithium-ion hybrid supercapacitor
Holey carbon nanolayer
Targeted porosity
High power density
High energy density

ABSTRACT

Lithium-ion hybrid supercapacitor emerges as a promising candidate to bridge the performance gap between lithium ion batteries and supercapacitors. However, for current lithium-ion hybrid supercapacitor systems, high energy storage is usually accompanied with the sacrifice of high power density due to the mismatched kinetics between the sluggish lithium intercalation in anode and the rapid ion adsorption/desorption at cathode. In this work, we design a simple and controllable synthesis of holey carbon nanolayers with targeted porosity as both anode and cathode to achieve rapid electrochemical kinetics in lithium-ion hybrid supercapacitors. The mesoporous structure, enlarged interlayer spacing and excellent electrical conductivity of anode ensure greatly mitigated lithium diffusion. Simultaneously, the hierarchical porous texture and large external active surface area of cathode contribute to an outstanding capacity of 140 mAh g⁻¹ and better rate capability. The lithium-ion hybrid supercapacitor based on holey carbon nanolayers shows a high energy density up to 181 Wh kg⁻¹, and still preserves a remarkable energy density of 114 Wh kg⁻¹ even at an ultra-high power density of 65 kW kg⁻¹. This work illustrates the pertinence of porosity and morphology manipulation as a competitive strategy for rational fabrication of lithium-ion hybrid supercapacitor electrodes with high power density.

1. Introduction

The race to develop cutting-edge technologies that underpin high-power electronic devices and electric vehicles has intensified concerns across wide swathes of the society and engendered escalating demands for reliable electricity storage solutions [1,2]. In this context, supercapacitors (SCs) with high power density and long life span represent one attractive alternative, which store charges mainly through the reversible ion adsorption at the electrode/electrolyte interface [3–5]. However, the large-scale application of SCs are still greatly hampered by their intrinsic low energy density (< 10 Wh kg⁻¹) when compared with the state-of-art lithium-ion batteries (LIBs) utilizing faradaic

lithiation/delithiation to deliver a sizeable energy density (~200 Wh kg⁻¹) [6,7]. Thus there exists a major thrust in promoting next-generation supercapacitors capable of both high-power and high-energy handling.

Since its advent in 2001, lithium-ion hybrid supercapacitor (LIHS), which shrewdly conjugates a large-capacity anode capable of reversible Li⁺ intercalation and a carbon-based fast-rate capacitive cathode, emerges as a promising candidate to integrate the complementary features of high-energy LIBs and high-power SCs [8–10]. Several recent researches on LIHSs reported high-level energy density up to 150–200 Wh kg⁻¹, ushering a great leap forward in comparison with their supercapacitor counterparts [11–13]. Nevertheless, current LIHS

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systems still suffer from a power predicament. In most of these reported LIHS cases, high energy density can only be achieved at the cost of low power output ($< 5 \text{ kW kg}^{-1}$) [14,15], which should be attributed to the mismatched kinetics between the sluggish lithium intercalation in anode and the swift ion adsorption at the cathode/electrolyte interface. To mitigate the rate-discrepancy is of utmost importance for high-power LIHSs.

For anode materials in LIHSs, the key limitation is the “either-or” dilemma between high capacity and high power capability because the rate performance related with Li^+ intercalation processes is greatly jeopardized by the slow Li^+ diffusion rate in the solid phase of electrode [16]. To date, though much research effort has been energetically devoted to the development of novel anode materials, the power plight still remains a largely unscathed scientific bottleneck in LIHS research. Anodes relying on alloying/dealloying processes (such as Si [15], Sn [17] and SnO_2 [18]) or conversion reactions (including MnO [19], Co_3O_4 [20], Fe_3O_4 [12], etc.) can provide high theoretical capacity ranging from 700 to 3600 mAh g^{-1} , but the large volume variation and poor kinetics during prolonged charge/discharge bring about inferior rate capability, severe electrode polarization and high capacity fading. Other insertion-type anodes like graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [21], $\text{H}_2\text{Ti}_6\text{O}_{13}$ [22], V_2O_5 [23], TiO_2 [14] and Nb_2O_5 [24] usually exhibit low specific capacity ($< 400 \text{ mA h g}^{-1}$) or high lithiation voltage plateau, leading up to restricted energy density. Unfortunately, another on-going affliction for high-power LIHSs is that the cathode materials based on commercial activated carbon (AC) faces inferior capacitive performances (30–40 mAh g^{-1}) particularly at high-power operations, because the ion transportation through the tortuous channels in microporous AC causes restricted kinetics and insufficient utilization of the electrode surface. This inevitably neutralizes the large capacity of battery-type anode, resulting in lower energy density as well as poor power capability of LIHSs. Therefore, it is urgently required to leverage synergetic kinetics in both cathode and anode of LIHSs toward efficient energy storage/release.

Targeted design of nanomaterials has been envisaged as a pivotal approach to tackle the kinetic imbalance between cathode and anode materials [25–27]. In order to secure high power performance in LIHS anode, the key solution is to facilitate Li^+ intercalation and transportation through regulating the nano-architecture of electrode materials. In this regard, layered mesoporous carbon materials with interconnected pore channels and expanded interlayer spacing can relieve ion diffusion kinetics, which make possible both high lithium storage capacity and high rate capability [28]. Moreover, the layered structure stacked within each other can effectively accommodate the volume change caused by repeated Li intercalation during cycling, contributing to the stabilized electrochemical behavior of anode [29]. Additionally, the high electrical conductivity of carbon materials can also help to minimize the equivalent series resistance and further improve the power density. With regard to cathode materials of LIHSs, large specific surface area must be considered to ensure high electrochemical utilization of the capacitive material, and an optimized porosity is favorable to forming conductive pathway to enhance ion transport rate. To fulfill this target, hierarchically porous carbon nanolayers are preferable to acquire high capacitive behavior especially at high rates due to their high surface area and shortened pore length [30,31]. In view of the above considerations, one appealing approach to fabricate high-performance LIHS systems is using carbon nanolayers with designed porosity to directly achieve high power output together with high-level energy storage; however, there has been little discussion for carbon nanolayers as electrode materials in LIHSs.

Herein, we have designed a simple and controllable synthesis of holey carbon nanolayers (HCNs) with targeted porosity and tailor-made morphology as both cathode and anode of LIHSs. It is demonstrated that the microstructure and pore arrangement of HCNs can be easily engineered to obtain an increased specific surface area, enlarged carbon interlayer spacing and enhanced electrode kinetics. The HCN-based

anode exhibits large Li-ion storage capacity and good charge/discharge rate within a wide potential window (0.03–3 V vs. Li/Li^+), while the high specific surface area ($2798 \text{ m}^2 \text{ g}^{-1}$) and hierarchical porosity of HCN-based cathode contribute to a high capacity of 140 mAh g^{-1} . As expected, the HCN-based LIHS electrodes show a high energy density of 181 Wh kg^{-1} at a power density of 650 W kg^{-1} , and more importantly, a remarkable energy density of 114 Wh kg^{-1} can still be preserved even at an ultra-high power density of 65 kW kg^{-1} . Furthermore, the HCN-based LIHS system exhibits an excellent capacity retention of 96% after 5000 cycles.

2. Experimental section

2.1. Synthesis of holey carbon nanolayers

A facile template method was firstly used to produce porous carbon precursors. 5 g Glucose (analytical grade) and 10 g MgO (analytical grade) were thoroughly mixed in 100 ml acetone and then dried at 70 °C for 12 h. The glucose/MgO mixture was carbonized in Ar (100 sccm) at 800 °C for 1 h. The black-color products were immersed in 1 M HCl solution to remove the MgO template, which was then filtered and spray-dried. A controllable chemical activation protocol was further used to prepare holey carbon nanolayers (HCNs) as electrode materials. Briefly, 0.5 g porous carbon precursor and a fixed amount of KOH (analytical grade) were stirred vigorously in 50 ml H_2O and then freeze-dried. Activation was conducted in Ar (100 sccm) at 800 °C for 1 h. The obtained products were treated in 1 M HCl, filtered and spray-dried, which were denoted as HCN-n for convenience (n represents the mass ratio of KOH and carbon precursor in the activation process).

2.2. Characterization methods

The scanning electron microscopy (SEM) observation and energy dispersive X-ray spectroscopy (EDS) mapping was conducted on a Hitachi S-4800 operating at an accelerating voltage of 20 kV. The samples were sonicated in ethanol and then dipped onto silicon plates before SEM analysis. Transmission electron microscopy (TEM) characterization were conducted on a JEOL JEM-2100F equipped with selected area electron diffraction (SAED). The accelerating voltage was set at 200 kV. Samples for TEM analysis were prepared by dipping a drop of sample/ethanol dispersion onto ultrathin amorphous carbon-coated copper grids and drying at room temperature for 1 h to completely evaporate the solvent. X-ray diffraction (XRD) patterns were done on a multifunctional Bruker D8 X-ray diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) at a scanning rate of 10° per minute. Micro Raman was recorded on a confocal Raman system (LabRam HR-800, Horiba Jobin Yvon) with excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) analysis was measured with a PHI Quantar SXM with Al as anode probe in $6.7 \times 10^{-8} \text{ Pa}$ to analyze the chemical composition of the samples. Electrical conductivity measurement was performed on a four-probe electrical conductivity instrument by pressing HCN powder under 6 MPa into a platelet. The nitrogen adsorption/desorption measurements were carried out on a Micromeritics ASAP 2020 HD Analyzer at 77 K. Prior to adsorption/desorption tests, the samples were degassed at 150 °C for 12 h with vacuum pumping. Specific surface area based on Brunauer-Emmett-Teller (BET) theory was calculated from the adsorbed amount of N_2 at the relative pressure of P/P_0 below 0.3. Pore size distribution was calculated according to Barrett-Joyner-Halenda (BJH) model and density function theory (DFT). Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 F3 Tarsus with a heating rate of 5 °C min^{-1} in N_2 atmosphere from 50 to 800 °C.

2.3. Electrochemical measurements

For the fabrication of working electrode, 80 wt% active material,

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