Research Paper

A high-power lithium-ion hybrid electrochemical capacitor based on citrate-derived electrodes

Xiaoliang Yu[a,c], Jiaojiao Deng[b], Changzhen Zhan[b], Ruitao Lv[b], Zheng-Hong Huang[a,b,*], Feiyu Kang[b,c,*]

[a] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[c] Engineering Laboratory for Functionalized Carbon Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

A B S T R A C T

Achieving high-power lithium-ion hybrid electrochemical capacitor (Li-HEC) through facile and low-cost synthesis procedures is still quite challenging. In this work, starting from daily used food additives, nitrogen-doped hierarchical porous carbon (N-HPC) was prepared through facile pyrolysis of magnesium citrate and subsequent NH_3 treatment, and carbon-coated Fe_2O_3 (Fe_2O_3@C) was synthesized by thermal decomposition of ferric citrate and following heat treatment in air, respectively. As-prepared N-HPC and Fe_2O_3@C were separately employed as cathode and anode materials to fabricate a high-power, which delivers a high energy density of $65 \, W \, h \, kg^{-1}$ at $368 \, W \, kg^{-1}$, and $31 \, W \, h \, kg^{-1}$ at a high power density of $9.2 \, kW \, kg^{-1}$. And it remains 84.1% capacity over 1000 galvanostatic charge-discharge cycles at $1 \, A \, g^{-1}$.

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1. Introduction

Supercapacitors (SCs) and lithium ion batteries (LIBs) are two promising technologies for electrochemical energy storage. SCs can achieve high power delivery by fast ion adsorption/desorption at the electrode/electrolyte interface, while LIBs enable high energy storage through bulk intercalation and conversion reactions between lithium and electrode materials [1,2]. Recently, combining two charge storage mechanisms in one device to fabricate lithium-ion hybrid electrochemical capacitors (Li-HEC) is being extensively explored, which is expected to bridge the performance gap between SCs and LIBs [3,4].

Energy density and power density are the two most important performance parameters for Li-HEC. The energy density can be improved by enhancing the specific capacity of capacitor-type porous carbon electrode and extending the potential window of the hybrid system. On the other hand, how to improve the high-power performance is still not so clear. According to the charge storage mechanism, the high-rate capability of the hybrid system can be determined by the sluggish redox reaction of battery component. Therefore, a lot of research works have been conducted to prepare high-rate battery-type electrode materials in order to achieve high power density of Li-HEC [5–8]. However, we can also see many examples in which such strategy does not work well. For instance, Lee et al. developed Nb_2O_5@carbon core-shell nanocrystals which can operate at a high current density of $5 \, A \, g^{-1}$ and maintains 50% capacity [9]. But when such high-rate anode was combined with activated carbon to construct Li-HEC device, the capacity retention at high rate is even lower than that of the LIB counterpart. Similar phenomenons have also been observed in other electrode materials, like $Li_4Ti_5O_{12}$ [10], Fe_3O_4 [11], $TiNb_2O_7$ [12], and so forth.

Besides, our previous investigation found that, unlike the general understanding that the Faradaic battery-type anode is the power-determining factor, the electric conductivity of porous carbon electrode can also significantly affect the high-rate performance of Li-HEC system [13,14]. Based on these, we can infer that it is the synergistic effect of both cathode and anode that determine the high-rate capability of the hybrid system. Therefore, rational design of both cathode and anode materials are of great significance to acquire high-power Li-HEC. Another issue in Li-HEC

research is that the synthesis strategies of two electrode materials are still somewhat complex and cost-expensive. Thus facile and scalable preparation of both electrodes at low costs is highly desirable.

Citrates are commonly used food additives in our daily life. In this communication, magnesium citrate and ferric citrate were employed separately to prepare nitrogen-doped hierarchical porous carbon (N-HPC) and carbon-coated Fe_2O_3 (Fe_2O_3@C) through facile two-step heat treatment. As-prepared N-HPC and Fe_2O_3@C materials can be used to fabricate a high-power Li-HEC.

2. Experimental

For synthesis of N-HPC, magnesium citrate was put in a tubular furnace and heat treated at 220, 350, 435 °C for 1 h and then 850 °C for 2 h in nitrogen. The heating rate is 2 °C min^{-1}. After acid washing and following NH_3 treatment at 800 °C for 2 h with a heating rate of 5 °C min^{-1}, target sample N-HPC was obtained. Ferric citrate was pyrolyzed by the same procedure to get Fe@C. After following heat treatment at 600 °C for 1 h in air with a heating rate of 5 °C min^{-1}, Fe_2O_3@C was prepared.

The microstructure was observed through transmission electron microscopy (TEM, Tecnai G20, 200 kV). The crystal structure was confirmed by X-ray diffraction (XRD, D8 Advance, Cu Kα radiation). Nitrogen adsorption-desorption test was conducted to evaluate the porosity porosities of samples (BELSORP-max). The surface property was investigate by X-ray photoelectron spectroscopy (XPS) (PHI Quantera Imaging).

Porous carbon electrode was prepared by coating aluminum foil with 75% N-HPC, 15% PVDF and 10% carbon black. The battery anode was produced by coating copper foil with 80% Fe_2O_3@C, 10% PVDF and 10% carbon black. The mass loading of N-HPC electrode is in the range of 2.1–2.7 mg, and the mass loading of Fe_2O_3@C electrode is in the range of 0.7–0.9 mg. Supercapacitor, LIB half cell and Li-HEC device were assembled by fabricating N-HPC//N-HPC, Fe_2O_3@C//lithium metal and N-HPC//Fe_2O_3@C, respectively. Pre-lithiation was performed by one full charge/discharge cycle followed by a charging process down to a certain potential in the second cycle. Land battery tester (CT2001A, China) and Arbin-BT2000 were used to perform the galvanostatic charge/discharge (GC) tests. Cyclic voltammetry (CV) tests were performed in VSP-300 electrochemical interface. The voltage windows for supercapacitor, LIB and Li-HEC systems were 0–2.7 V, 0.01–3 V and 1–4 V, respectively. The electrolyte used in all system was 1 M $LiPF_6$ in EC/DEC (1:1 by volume).

3. Results and discussion

Fig. 1 schematically illustrates the synthesis procedures of two electrode materials and fabrication process of the hybrid system. Citrates consist of two segments, the organic segment and metal ion segment. During pyrolysis of citrates under inert atmosphere, the organic segment polymerized and decomposed to form the amorphous carbon matrix. At the mean time, metal oxides/metal (MgO/Fe) nanocrystals were generated and randomly distributed in the carbon matrix. After following heat treatment in NH_3 or air, N-HPC cathode material or Fe_2O_3@C anode material can be obtained.

Fig. 2 shows the microstructure and capacitive performance of N-HPC cathode. Nitrogen adsorption-desorption test was conducted to evaluate the porosity porosities of samples and the results are shown in Fig. 2a. The specific surface area and pore size distribution (PSD) were estimated from Brunauer-Emmett-Teller method and density functional theory, respectively. N-HPC shows a hybrid of type-I and type-IV isotherm, suggesting that its carbon framework is dominantly mesoporous. The inset is the corresponding PSD curve, which displays multimodal distributions. The micropores and small mesopores (< 4 nm) should be generated by pyrolysis of organic, while large mesopores are formed from the removal of MgO nanocrystals. The specific surface area and pore volume are calculated to be as high as 1290 m^2 g^{-1} and 3.04 cm^3 g^{-1}. XPS measurement was conducted to investigate the surface property of N-HPC and the result is shown in Fig. 2b. Through quantitative analysis, a high nitrogen content of 3.6% can determined. The abundant nitrogen-containing surface groups are advantageous to enhancing the electric conductivity of the carbon framework and raising the wettability of porous surface in the electrolyte [15]. In order to investigate the electrochemical performance of N-HPC, symmetric supercapacitor was assembled and the test results are shown in Fig. 2c and d. The GC curves in Fig. 2c are in isosceles triangle shape, indicating its electric double-layer capacitive behavior. Fig. 2d shows the rate performance of N-HPC in comparison with commercially available microporous YP-17D. N-HPC displays a good high-rate capability with a high specific capacitance of 101 F g^{-1} at 0.1 A g^{-1} and 67% capacity retention even at 20 A g^{-1}, which enormously outperforms that of YP-17D. The better rate performance can be ascribed to the smooth ion diffusion channel of N-HPC as well as its higher electric conductivity in comparison with YP-17D (see Fig. S1).

Fig. 3 shows the microstructure and electrochemical performance of Fe_2O_3@C anode. From the TEM image in Fig. 3a, we can observe many iron@ graphitic carbon layer core-shell nanoparticles with different particle sizes, which are irregularly
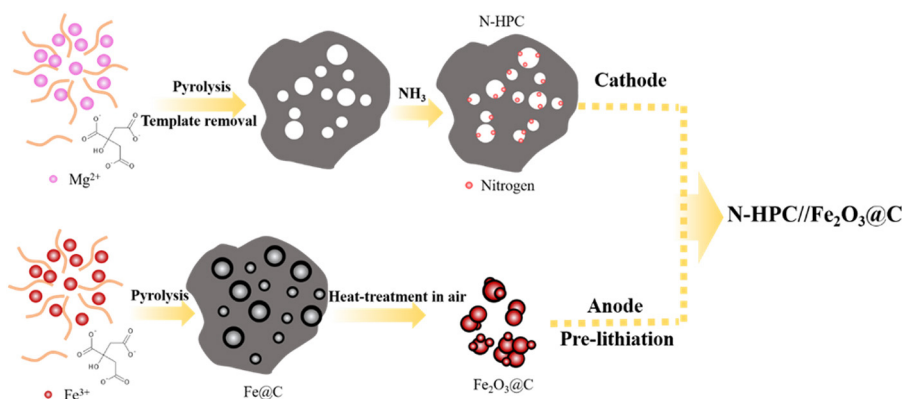

Fig. 1. Preparation process of two electrode materials and the Li-HEC device.