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Synthesis of Sodium-vanadate-doped Ordered Mesoporous Carbon Foams as Capacitor Electrode Materials

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Sodium-vanadate-doped ordered mesoporous carbon foams (V-MCFs) were prepared through an evaporation-induced self-assembly strategy. The resultant V-MCFs exhibit highly ordered mesostructure with specific surface areas of 714 $m^2\,g^{-1}$ and uniform pore sizes of 4.1 nm. The surface wettability and graphitization degree of V-MCFs were increased due to the incorporation of sodium vanadate into the carbon matrix. Besides, sodium vanadate brings a pseudo-capacitive effect in V-MCFs. V-MCFs thus exhibit higher capacitance and fast charge–discharge properties compared with pure mesoporous carbon foams.

The importance of energy-storage devices has been constantly growing with the increasing popularity of various portable electronic devices and motor vehicles. In recent years, electric double-layer capacitors (EDLCs) have been extensively investigated for use in high-power sources due to their high charge utilization and fast charge storage.[1–3] Activated carbons are carbon materials suitable for application as electrodes in EDLCs because of their high surface area.[4] But the small disordered micropores of these carbons cannot be readily accessed by the electrolyte and also constrict the space for charge accommodation inside the pore wall, which limit their gravimetric capacitance. Compared with activated carbon, mesoporous carbon foams (MCFs)[5] which possess relatively large size-controllable mesopores can facilitate the ion diffusion and usually show much better rate capability. Therefore, they have been considered as promising electrode materials for EDLC use because of the highly available charge-storage sites on the pore surfaces.[6] However, the specific capacitance is usually limited for their low electrical conductivity and relatively inert surface and poor wettability. To enhance the electrochemical properties, various compounds were introduced into the MCFs.[7–15] For instance, loading or doping metal and metal oxides such as silver,[9] platinum,[10] ruthenium oxides,[11] and manganese oxides[12] in the MCFs have been reported and proven to have a higher capacitance. Yu et al.[13] and Hu et al.[14] artificially loaded vanadium oxides on the surface of MCFs through ultrasonic synthesis and solid-state reaction process, respectively. Because of the multiple valence state of vanadium, vanadium-oxide-doped MCFs show good capacitive performance. But vanadium oxides are unstable in concentrated acid or alkali, these materials can only be used in neutral solutions, which would partly restrict their industrial application as capacitor electrode materials.

In this letter, we report the synthesis of sodium-vanadate-doped ordered mesoporous carbon foams (V-MCFs) through an evaporation-induced self-assembly approach. During the synthesis, the sodium vanadate was embedded in the pore walls and the electrode obtained from V-MCFs can be used in 6 mol L^{-1} KOH electrolyte. Compared with pure MCFs, V-MCFs exhibit higher capacitance and fast charge–discharge characteristics resulting from the improvement of graphitization, surface wettability, and pseudo-capacitive effect[16,17] of sodium vanadate incorporated in the carbon matrix.

V-MCFs were prepared by using resol as an organic precursor, NaOH as a catalyst, $NaVO_4$ as an inorganic precursor, and triblock copolymers Pluronic F127 ($M_w = 12600$, EO_{106}–PO_{70}–EO_{106}) as a template. The resol was prepared according to a procedure described in ref 18. Typically, 1.00 g of F127 and 0.03 g of $NaVO_4$ were dissolved in 25 mL of ethanol. Then 5.00 g of resol precursors in ethanol solution containing 0.61 g of phenol and 0.39 g of formaldehyde was added to the above mixture. A homogeneous solution was obtained after stirring for 20 min. The solution was coated by a thin polymer membrane on the surface of a dish, and the membrane was kept at 25 °C for 8 h. Thermal polymerization of the membranes was carried out at 100 °C for 12 h. The thin membrane was crushed into powders and carbonized at 850 °C in a purified nitrogen flow with a heat rate of 1 °C min^{-1} to decompose the surfactant template and to obtain V-MCFs. As a comparison, we synthesized MCFs by similar approach without inorganic precursor.

Figure 1 shows the nitrogen adsorption and desorption isotherms and pore size distribution curves. The isotherms of V-MCFs show representative type IV curves[19] which exhibit a sharp capillary condensation step at relative pressures of 0.4–0.8, corresponding to the narrow pore-size distribution. The V-MCFs have a Brunauer–Emmett–Teller (BET) surface area of around 714 $m^2\,g^{-1}$. The pore-size distribution of V-MCFs is

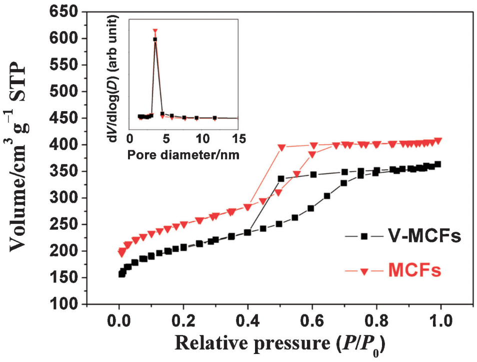

Figure 1. Nitrogen adsorption and desorption isotherms and the pore-size distributions (insert) of V-MCFs and MCFs.

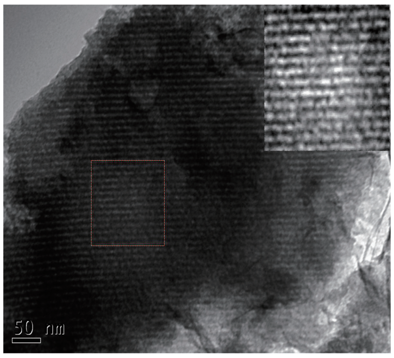

Figure 2. TEM photograph of V-MCFs.

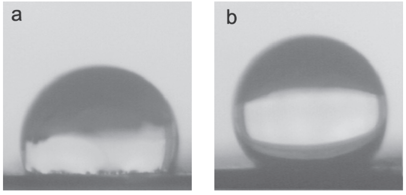

Figure 3. Photographs of water droplet on the surface of V-MCFs (a) and MCFs (b).

calculated from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method, and it exhibits single pores with the most probable pore size of 4.1 nm. For comparison, MCFs possess a BET area of 856 $m^2 g^{-1}$ and with the most probable pore size of 3.9 nm. These results reveal that V-MCFs have mesoporous structure and possess uniform pore size, that 4.3% mass ratio of sodium vanadate was embedded in the pore walls, and that the incorporation of sodium vanadate has no obvious influence on the framework of V-MCFs. Figure 2 shows the transmission electron microscopy (TEM) image of V-MCFs. It indicates that V-MCFs have highly ordered mesostructure with uniform pores and that the individual pore size is around 4 nm, which matches the results of nitrogen adsorption and desorption.

The surface wettability of V-MCFs and MCFs have been investigated by measurement of the water contact angle. Figure 3 shows the shape of a water droplet on the surface of V-MCFs and MCFs. The contact angle of V-MCFs for water is about 112.9°, obviously lower than that of MCFs (132.8°), which shows the surface wettability of V-MCFs is improved by the introduction of sodium vanadate into the carbon matrix.

The Raman spectra of V-MCFs and MCFs are displayed in Figure 4. The spectra shows a distinct pair of broad bands near 1591 (G band) and 1361 cm^{-1} (D band). The G band and D band are assigned to the hexagonal carbon plane and crystal defects or imperfections, respectively.[20,21] The ratio of the relative intensity of these two band (I_D/I_G) is proportional to the number of defect sites in the graphite carbon. The lower the ratio is, the higher the graphitization is.[22] It can be calculated that the I_D/I_G ratio declines from 1.0 (MCFs) to 0.9 (V-MCFs). These results reflect that the graphitization degree increased with the incorporation of sodium vanadate into V-MCFs.

The improved wettability and higher graphitization rate are expected to increase the electrochemical properties of V-MCFs. Figure 5 shows the cyclic voltammetry (CV) curves of V-MCFs and MCFs electrodes.[23] The two materials are stable in the potential ranges of −0.8 to 0 V. The CV curves of V-MCFs were characterized with rectangle-like shape at scanning rate from 10 to 50 $mV s^{-1}$, which indicates an ideal capacitance behavior in a very quick charging/discharging process in V-MCFs. However, the CV curve of MCFs veered away much from rectangle-shape at a scanning rate of 50 $mV s^{-1}$, suggesting resistance-like electrochemical behavior. The improvement of CV performances of V-MCFs should be ascribed to their higher graphitization degree and consequent conductivity. The capacitance of material is in proportion to the areas of its CV curves; it can be observed that the capacitance of the V-MCFs is larger than that of MCFs.

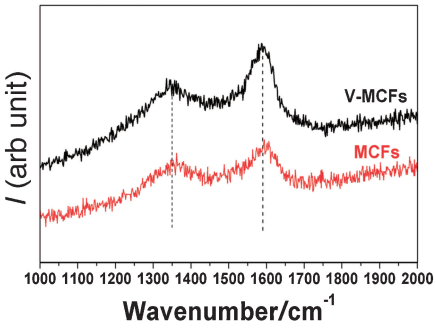

Figure 4. Raman spectra of V-MCFs and MCFs.

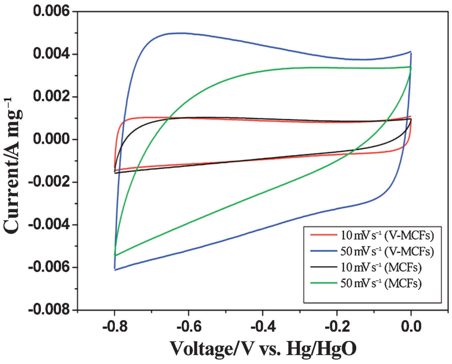

Figure 5. Cyclic voltammetry curves of V-MCFs and MCFs.

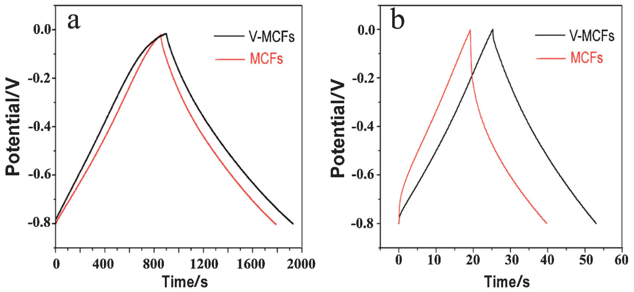

Figure 6. Galvanostatic charge–discharge curves of V-MCFs and MCF electrodes at the loading current density of 100 $mA g^{-1}$ (a) and 3 $A g^{-1}$ (b).

The galvanostatic charge–discharge behavior further reflects electrical energy storage.[24] Figure 6 exhibits galvanostatic charge–discharge curves of V-MCFs and MCFs electrodes at different loading current density. Both V-MCFs and MCF electrodes present linear galvanostatic charge–discharge curves at the loading current density of 100 mA g^{-1}. The calculated specific capacitance from −0.2 to −0.6 V of the V-MCFs reaches 128 F g^{-1}, higher than that of the MCFs (115 F g^{-1}). With the increase of current densities to 3 A g^{-1}, the specific capacitance of V-MCFs decreases to 105 F g^{-1}, still higher than that of MCFs which is 77 F g^{-1}. And the symmetriculness of charge–discharge curve of V-MCFs is better than that of MCFs. Furthermore, the equivalent series resistance of V-MCFs calculated from the ohmic drop at the beginning of the discharge was obviously less than that of MCFs. These results proved that, compared with MCFs, the specific capacitance performance of V-MCFs was significantly improved, especially at high current density. The enhancement of the electrochemical properties is attributed to improved wettability and consequent enhancement of surface contact of electrolyte and carbon, increased graphitization degree, as well as the pseudo-capacitance through additional faradic reactions arising from sodium vanadate.

In conclusion, highly ordered V-MCFs with BET surface areas of 714 $m^2 g^{-1}$ and uniform pore sizes of 4.1 nm were prepared by evaporation-induced self-assembly. V-MCFs exhibit higher capacitance and fast charge–discharge properties compared with MCFs. The enhancement of the electrochemical properties of V-MCFs results from the improved surface wettability, increased graphitization degree, and the pseudo-capacitance effect through additional faradic reactions arising from sodium vanadate. It can be expected that V-MCFs are promising for application in supercapacitors.

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23 The electrochemical measurements were done in a three-electrode experimental setup. Hg/HgO electrode was used as reference electrode, and nickel foil as the counter electrode. The working electrode was prepared as follows: V-MCFs or MCFs were mixed with poly(tetrafluoroethylene) and graphite with a mass ratio of 8.5:1:0.5. The mixture was pressed between two pieces of nickel foam under 30 MPa. Thereafter, the 0.45-mm-thick electrode was dried overnight at 100 °C. Cyclic voltammograms and galvanostatic charge–discharge behavior were tested in electrolyte of 6 mol L^{-1} KOH using a CHI 660D system.

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