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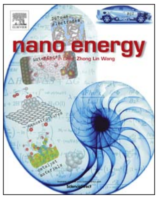

Full paper

Dual electronic-ionic conductivity of pseudo-capacitive filler enables high volumetric capacitance from dense graphene micro-particles

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ABSTRACT

Volumetric performance is highly important for evaluating the potential of supercapacitors, especially for the case where electrode space is limited. To achieve high space utilization, the less pores to be included the better. Along this direction, we showed previously a PANI/graphene composite almost free of porosity by shrinking the composite network to the most compact, which yet exhibited a high volumetric capacitance and a good rate capability. The PANI/graphene solid composite simultaneously enabled maximized space utilization of the electrode volume and achieved unimpeded ion transport, which seems counter to the general design principle of electrode materials where appropriate porous structure is highly desired. Here we propose the proton transport mechanism of PANI in the dense composite, which indicates that PANI is a dual electronic-ionic conductivity polymer that acts not only as a pseudo-capacitive active material for high energy storage but also as a proton conductor that realizes proton transport from the electrode/electrolyte interface to the inner of the dense micro-particles. More importantly, we further propose the design principle of non-porous carbon-based composites to achieve high volumetric performance, in which a good dual electronic-ionic conductor is selected as the best pseudo-capacitive filler. This work inspires new insights into better design and preparation of the composite electrodes for compact energy storage devices.

1. Introduction

Energy storage device is going smaller, portable and more energetic. This raises growing concerns over the volumetric performance of electrode materials for electrochemical energy storage [1–9]. Due to their high power density and long cycle life, supercapacitors are considered to be among the most promising energy storage devices [1,3,6,10]. In general, metal (metal oxide or hydroxide)-based electrode materials could deliver high volumetric capacitance, which is mainly attributed to their intrinsically high densities [6,11–13]. However, the relatively low conductivity and porosity of the metal-based electrode materials restricted their performance scalability. Comparatively, metal-free electrode materials with abundant porosity, high chemical activity and electronic conductivity show better performance scalability and sustainability in energy storage devices [3,14–23]. Nevertheless, most of the metal-free electrode materials such as carbon materials possess low packing densities [24–30]. Densifying of carbon network could effectively increase the density of carbon materials, but the dense carbon materials still retain some amount of porosity [14]. In order to further increase the specific capacitance and the space utilization rate of the electrodes, pseudo-capacitive materials are often incorporated into porous carbon materials [12,13,15,31–35]. If a pseudo-capacitive material partially filled into the dense carbon materials, the density and gravimetric capacitance could be increased at the same time. However, how to achieve the dense carbon material fully filled with pseudo-capacitive materials without sacrificing its gravimetric capacitance is still a challenge (Scheme 1).

In our previous work, we prepared a high density porous graphene monolith with a density up to 1.58 g $\mathrm{cm^{-3}}$ through capillary evaporation induced drying process, which could deliver a volumetric capacitance of 376 F $\mathrm{cm^{-3}}$ [14]. The graphene monolith still have 30% of porosity with specific surface area up to 370 $\mathrm{m^2\,g^{-1}}$. If a pseudo-capacitive soft material is filled into the pores of graphene monolith, the graphene framework could provide electron percolation to the

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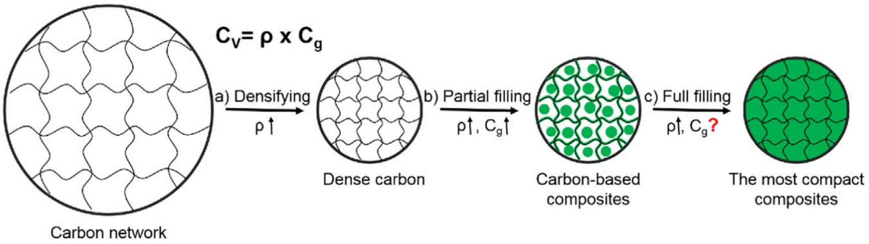

Scheme 1. The design principle of carbon based composite materials for high volumetric performance. (a) Densifying of carbon network increases volumetric performance; (b) Pseudo-capacitive materials partially filled into dense network further increase volumetric capacitance; (c) How to achieve the dense network fully filled with pseudo-capacitive materials without sacrificing its gravimetric capacitance is still a challenge.

fillers and may also help confine the fillers to improve their electrochemical stability [36–41]. Indeed, when PANI was chosen as the soft filler for the graphene monolith, the density of the PANI/graphene composites with 54 wt% PANI loading was maintained over 1.5 g cm^{-3} and the volumetric capacitance could be further increased to 800 F cm^{-3}, which is the highest value for metal-free supercapacitor materials with high stability [15]. Surprisingly, assuming the density of graphene monolith remains unchanged in the composite, the density of PANI is about 1.4 g cm^{-3} which is close to its theoretical density value in the emeraldine salt form [42]. This is to say, the PANI/graphene composite was shrinking to the most compact structure and the pores and channels of the graphene monolith were fully filled with PANI. As a strong evidence for this, the specific surface area of the capillary dried composite is demonstrated as almost zero, which is in a sharp contrast to 150 $m^2\,g^{-1}$ of the freezing dried composite. The results of the methylene blue solution adsorption are in consistent with the nitrogen adsorption/desorption measurements (Fig. S1), which further supports that the PANI/graphene composites are highly dense packing and almost free of porosity. Then an important question needed to be addressed is that as the PANI/graphene composites shrink to the most compact structure and almost free of porosity yet exhibit a high volumetric capacitance and good rate capability, how do the ion transport/diffuse rapidly in the highly dense micro-particles? Contrary to typical capacitive materials in which ions are transported to the inner of materials through electrolyte diffusion in the channels of electrode materials, the ion diffusion phenomenon in the dense PANI/graphene composite is more similar to the intercalation or conversion bulk redox reaction taking place in battery electrode materials.

Obviously, it is very useful to clarify the charge storage and ions transport mechanism of the dense PANI/graphene composite in the redox protonation/deprotonation processes. By comparing the capillary dried dense composite and freezing dried composite samples, we find that PANI is a dual electronic-ionic conducting polymer which could realize proton transport from the electrode/electrolyte interface to the inner of the dense micro-particles. The capillary dried dense PANI/graphene composite enables maximized space utilization rate of the electrode volume, which is critical for high volumetric performance supercapacitors.

2. Experimental section

2.1. Synthesis of PANI/graphene composites

Graphite oxide was prepared from graphite powder using a modified Hummers method as reported previously. GO hydrogel was prepared by one-step hydrothermal assemble process [14]. And the PANI/graphene composites were prepared by static adsorption and *in-situ* chemical polymerization method in our previous work [15]. Specifically, The GO hydrogel was immersed in 20 mL of 1 M HCl aqueous solution containing aniline (ANI) for 12 h to ensure the complete adsorption of ANI monomer. Then the resultant GO hydrogel was transferred into a 20 mL of 1 M HCl aqueous solution containing ammonium persulfate (APS). The polymerization was carried out at 0 °C for 2 h followed by the further reduction using hydroiodic acid (HI). Finally we obtained the PANI/graphene solid composite through capillary evaporation induced drying. In comparison, the 3D porous PANI/graphene foam composite was prepared by freezing dried processes.

2.2. Materials characterization

SEM observation was performed on Hitachi S-4800 (Hitachi, Japan). Nitrogen adsorption was conducted at 77 K using a BEL-mini instrument (BEL Inc., Japan), the specific surface area was obtained by Brunauer-Emmett-Teller (BET) analyses of the adsorption/desorption isotherm. UV–VIS spectrum (4802s, Unico, China) was used to detect the concentration of methylene blue solution. The density of the electrode material is the monolith's density determined by Archimedes principle with a balance (METTLER TOLEDO XS205) equipped with accessories for the density determination.

2.3. Electrochemical measurements

To prepare electrode, the solid composites were first pulverized to particle powder. The electrodes were prepared by mixing active materials with polytetrafluoroethylene (PTFE) and carbon black with a weight ratio of 90:5:5 in an ethanol solution. The mixture was kneaded into a paste, which was then pressed onto the stainless steel sheet. Generally, the loading mass of the electrodes containing binder and carbon black is *ca.* 3.0 mg cm^{-2}. All the electrochemical tests were carried out in a two electrode configuration. The symmetric supercapacitor was tested with a potential range from 0 to 0.8 V and 1 M H_2SO_4 aqueous solution was used as the electrolyte. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge-discharge measurements were conducted on the Eco Chemie Autolab 128N (Metrohm, Switzerland). EIS tests were carried out at the open circuit potential in a frequency range from 10 mHz to 10 kHz. The gravimetric and volumetric capacitances of one electrode were calculated from galvanostatic charge/discharge curves using the following equations:

$$C_s(Fg^{-1}) = \frac{2I\Delta t}{m\Delta V} \tag{1}$$

$$C_v(Fcm^{-3}) = \rho \times C_s \tag{2}$$

where C_s (F g^{-1}) is the gravimetric capacitance of the single electrode, C_v (F cm^{-3}) is the volumetric capacitance of the single electrode, I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the mass of a single electrode, and ΔV (V) is the potential window during the discharge process. ρ (g cm^{-3}) is the density of the electrode material.

3. Results and discussion

The PANI/graphene composites were prepared by an orientated polymerization of aniline followed by controlled shrinkage of graphene framework as reported in our previous work [15]. Specifically, the