



## Short communication

A novel activated mesocarbon microbead(aMCMB)/Mn<sub>3</sub>O<sub>4</sub> composite for electrochemical capacitors in organic electrolyte

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## ABSTRACT

A novel activated mesocarbon microbead(aMCMB)/Mn<sub>3</sub>O<sub>4</sub> composite is successfully prepared for electrochemical capacitors. The morphology and crystal structure of the composite are investigated by scanning electron microscopy and X-ray diffraction. The electrochemical studies indicate that the aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite has ideal capacitive performance in 1.0 mol L<sup>-1</sup> LiPF<sub>6</sub>(EC + DMC). A maximum specific capacitance of 178 F g<sup>-1</sup> is obtained for the composite via galvanostatic charge–discharge at a current density of 330 mA g<sup>-1</sup>, and the specific capacitance of Mn<sub>3</sub>O<sub>4</sub> is estimated to be as high as 445 F g<sup>-1</sup>. The aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite material exhibits ideal capacitive behavior indicating a promising electrode material for electrochemical supercapacitors.

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## 1. Introduction

Electrochemical capacitor or supercapacitor is a type of energy storage device, with features intermediate between conventional dielectric capacitors and batteries. According to the mechanism of charge storage, supercapacitor can be categorized as two types: electrical double-layer capacitor (EDLC) with activated carbon materials as electrodes, and the other is Faradic pseudo-capacitor with metal oxides or conducting polymers as electrodes.

Mesocarbon microbead (MCMB) as a promising carbon material gained much attention from many researchers, which can be used to fabricate activated carbons with high surface area [1–3]. RuO<sub>2</sub> is a high capacitance material for Faradic pseudo-capacitor, but the high cost of this precious metal is the major disadvantage for commercial applications. Consequently, much attention has been paid to low cost transition metal oxides, such as CoO<sub>x</sub>, NiO<sub>x</sub> and MnO<sub>x</sub>, in which MnO<sub>x</sub> is considered to be the most promising material for pseudo-capacitor, not only because of its low cost but also its environmental friendliness.

In recent years, carbon/metal oxide composites have gained much interest owing to their potential applications in supercapacitors requiring both high capacitance and long cycle life [4–7]. However, most of these studies about composites for supercapacitor are based on aqueous electrolyte. The operating voltage region is restricted to 1.23 V due to the thermodynamic electro-

chemical window of water, which limits the energy density of supercapacitor. One of the main ways to enhance energy density is to use organic medium as electrolyte because their decomposition potential window can reach 2–4 V. In this paper, we report a novel composite of aMCMB/Mn<sub>3</sub>O<sub>4</sub> for electrochemical capacitor in 1.0 mol L<sup>-1</sup> LiPF<sub>6</sub>(EC + DMC). To the best of our knowledge, this is the first reported assembly of capacitors with MCMB/metal oxide composite in organic electrolyte.

## 2. Experimental procedure

In this paper, the initial MCMB was purchased from Tianjin Tiecheng Battery Co. Ltd. in China with average diameter of 25 μm and the specific surface area 32.6 m<sup>2</sup> g<sup>-1</sup>. In order to improve the adsorption capacity and the specific surface area, the MCMB was heat treated by KOH with steps as follows [1]: the MCMB was mixed with KOH (6:1, w/w) in deionized water, and then the mixture was heated at 2 °C min<sup>-1</sup> up to 950 °C and was held for 1.5 h in Ar flow. After cooling, it was washed with 5 wt.% HCl and deionized water and then dried in vacuum, the product was denoted as activated mesocarbon microbeads(aMCMB). The typical preparation procedure for MCMB/Mn<sub>3</sub>O<sub>4</sub> composite was as follows: 0.8 g aMCMB powders were mixed with 50 ml 2.5 wt.% Mn(NO<sub>3</sub>)<sub>2</sub> in ethanol solution, the mixture was magnetically stirred for 4 h in room temperature so as to Mn(NO<sub>3</sub>)<sub>2</sub> was fully adsorbed on the surface of aMCMB. The obtained mixture was heated at 2 °C min<sup>-1</sup> up to 200 °C and was held for 1 h under the protection of Ar flow, the aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite was obtained finally. X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) were

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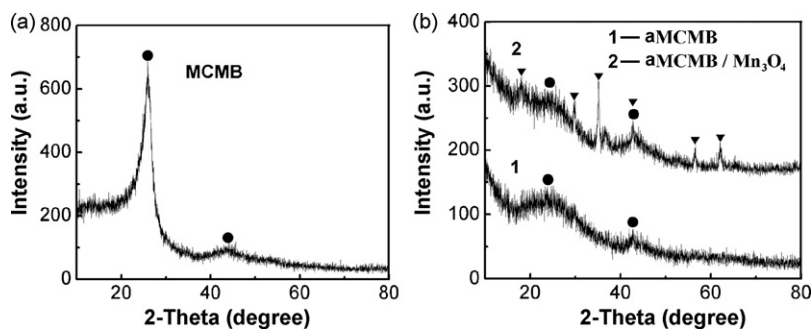


Fig. 1. XRD patterns of MCMB, aMCMB and aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite. The peaks of carbon and Mn<sub>3</sub>O<sub>4</sub> are noted with (●) and (▼), respectively.

carried out to study the morphology and phase structure of MCMB, aMCMB and MCMB/Mn<sub>3</sub>O<sub>4</sub> composite powders, respectively. An energy dispersion spectrometry (EDS) and ICP-AES were used to analyse the distribution and content of Mn<sub>3</sub>O<sub>4</sub> in the MCMB/Mn<sub>3</sub>O<sub>4</sub> composite.

In order to study the electrochemical performance, aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite and aMCMB was prepared into electrodes and assembled into capacitor cells, respectively. Firstly, the active substance was mixed with binder polytetrafluoroethylene (PTFE) (95:5, w/w) in ethanol, and was rolled into a film (80–100 μm thick), then the film was cut into disk electrodes with diameter of 10 mm. Finally, fastener-type symmetric electrochemical capacitor cells were assembled with a pair of identical electrodes and a piece of microporous separator between them. And 1.0 mol L<sup>-1</sup> LiPF<sub>6</sub> in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) was used for electrolyte. In order to investigate the electrochemical properties of capacitor, cyclic voltammetry (CV) was performed on an electrochemical workstation, cyclic voltammograms were recorded from 0.5 to 3.0 V. The charge–discharge

was conducted in the voltage range of 0–3.0 V with a battery tester at the specific current of 330 mA g<sup>-1</sup>. The specific capacitances of the electrodes are evaluated with the following formula:  $C_T = I \Delta t / \Delta V$ ,  $1/C_T = 1/m_1 C_s + 1/m_2 C_s$ , where  $C_T$  is total series capacitance of the two electrodes in electrochemical capacitor cell (F),  $I$  is the current (A),  $\Delta t$  is the discharging time (s),  $\Delta V$  is the voltage difference of discharge (V),  $C_s$  is the specific capacitance of a single electrode (F g<sup>-1</sup>),  $m_1$  and  $m_2$  are the active mass of the two electrodes, respectively.

### 3. Results and discussion

X-ray diffraction (XRD) patterns of the MCMB (a), as-prepared aMCMB (b-1) and aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite (b-2) are shown in Fig. 1. The pattern of MCMB before activation shows a wide peak at 23.8° (002) and a weak peak at 43.9° (101), indicating a certain crystalline structure of graphite. However, as shown in b-1 for aMCMB, the peak at 23.8° decreases sharply and peak at 43.9° is

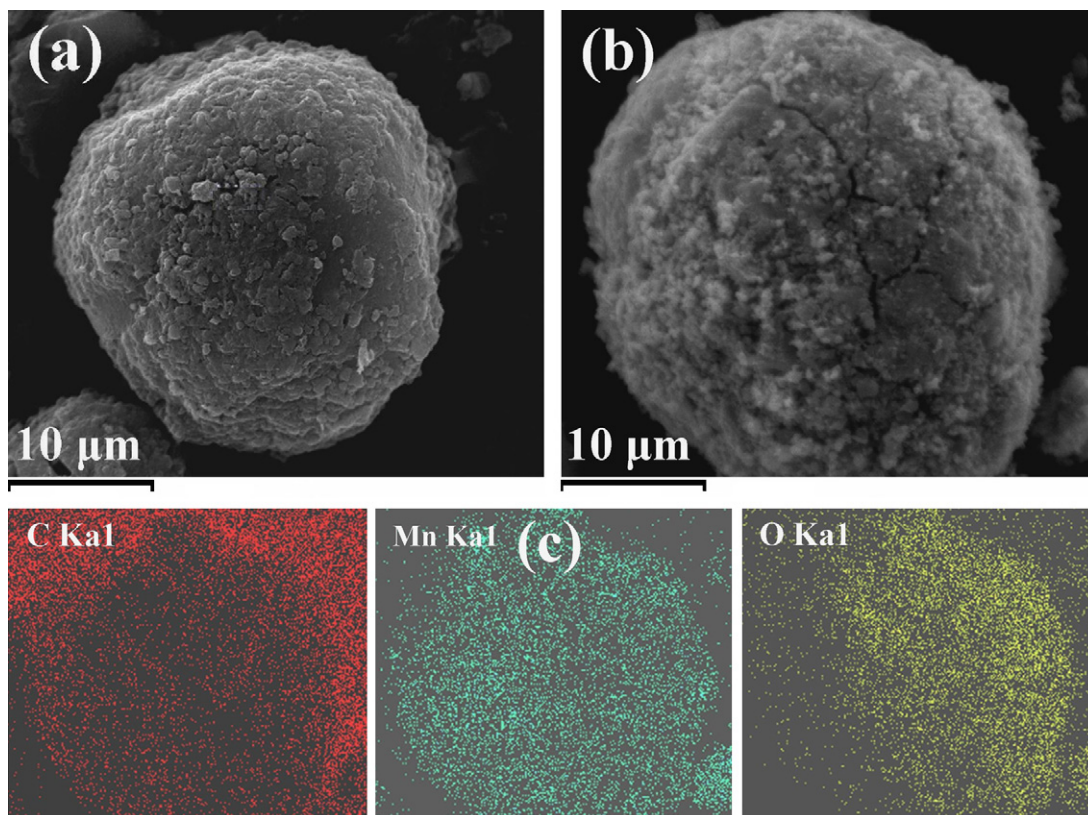


Fig. 2. SEM photographs of (a) aMCMB, (b) aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite, and (c) corresponding EDS pattern (mapping) of aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite.

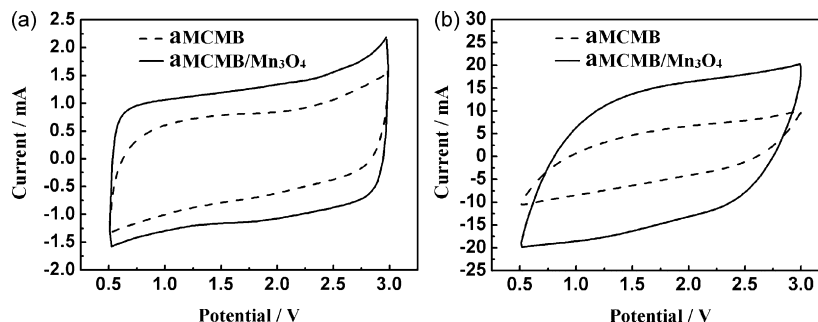


Fig. 3. Cyclic voltammograms of the aMCMB electrode and aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode with different scan rates: (a) 5 mV s<sup>-1</sup> and (b) 100 mV s<sup>-1</sup>.

also very weak, suggesting that after activation by KOH, MCMB has an amorphous structure [1,8,9] and the graphite crystallites are destroyed by K intercalation [10]. The amorphous carbon is more suitable for supercapacitor electrode material than the crystal structure, because the amorphous structure is conducive to the infiltration for electrolyte [10]. The pattern of the aMCMB/Mn<sub>3</sub>O<sub>4</sub> indicates that it is a typical amorphous structure, five weak peaks were assigned in 18.1°, 29.8°, 42.9°, 56.7° and 62.2°, and a strong peak in 35.1°, which was determined as pure Mn<sub>3</sub>O<sub>4</sub> (JCPDS No. 13-0162).

Fig. 2(a) and (b) are the SEM images of the aMCMB and aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite, respectively. As seen in Fig. 2(a), the MCMB after activation with a very rough surface was a result of KOH etching [1,11]. It can be obviously observed in Fig. 2(b), there are numberless manganese oxide particles about 200 nm dispersed uniformly onto the surface of aMCMB, and it was further illustrated by EDS pattern (mapping) from Fig. 2(c). The specific surface area of the treated aMCMB and aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite was 3290.4 and 3126.7 m<sup>2</sup> g<sup>-1</sup> determined from the application of the BET, indicating that the superficial performance of aMCMB had not been changed much more after adding Mn<sub>3</sub>O<sub>4</sub>, but the potential pseudo-capacitance may be impregnated for aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite.

Fig. 3 shows the cyclic voltammograms of aMCMB electrode and aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode, measured in 1 mol L<sup>-1</sup> LiPF<sub>6</sub>/(DMC+EC) solution, in potential range of 0.5–3.0 V, at different potential scan rates: (a) 5 mV s<sup>-1</sup> and (b) 100 mV s<sup>-1</sup>. Both of the electrodes exhibited good rectangular shapes at a relatively slow scan speed of 5 mV s<sup>-1</sup>, which indicate good capacitive performance [12,13]. When the scan rate increases to 100 mV s<sup>-1</sup>, the CV curve of aMCMB electrode is distorted while that of aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode still maintains a good rectangular shape, which suggest that the composite electrode has a more excellent reversibility than the simple aMCMB electrode.

The galvanostatic charge–discharge curves of electrodes were depicted in Fig. 4, (a) for aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode and (b) for aMCMB electrode. It shows that the operating voltage region is up to 3.0 V, using LiPF<sub>6</sub>/(DMC+EC) as electrolyte. At the current density of 330 mA g<sup>-1</sup>, the shape of the curve is closely linear and the charge and discharge curves show a typical triangle symmetrical distribution, all of which indicates the good capacitive properties of the materials. The specific capacitances ( $C_s$ ) were calculated from the discharging plots of  $E-t$  curves. The specific capacitance of aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode and single aMCMB electrode was 178 and 167 F g<sup>-1</sup>, respectively. According to analysis of ICP-AES, the content of Mn<sub>3</sub>O<sub>4</sub> in aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite is 3.98 wt.%, indicating that the specific capacitance based on Mn<sub>3</sub>O<sub>4</sub> is up to 445 F g<sup>-1</sup>, which was evaluated by deducting the capacitance of aMCMB electrode from total capacitance of aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode [14,15]:

$$C_{s-Mn} = \frac{C_{s-Com} - C_{s-C} \times M_C}{M_{Mn}}$$

where  $C_{s-Mn}$  is the specific capacitance of the aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode based on Mn<sub>3</sub>O<sub>4</sub>;  $C_{s-Com}$  and  $C_{s-C}$  are the specific capacitances of aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite and aMCMB electrodes, respectively;  $M_C$  and  $M_{Mn}$  are content of Mn<sub>3</sub>O<sub>4</sub> in aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite, respectively.

The microtexture of MCMB is usually considered to be global type or Brooks–Taylor type with regular lamellar structures [16,17]. According to XRD analysis, MCMB has an amorphous structure and the graphite crystallite is destroyed after activation by KOH. It is thought that K intercalates into the lamellae of the crystallites and expands the interlayer of the crystallites, and when K was washed away with water, the lamellae could not return to previous structure and form interlayer voids [2], and a porous structures can be formed finally. Shen and Xue [1] reported that a mesopore volume content higher than 50% was prepared successfully from the activation of MCMB with KOH. In this paper, the aMCMB was prepared by KOH according to Shen, it could be inferred that the high capacitance of 167 F g<sup>-1</sup> for aMCMB mainly attributed to the special porous structure of aMCMB for forming electrical double-layer capacitance.

Recently, Dubal et al. [18] reported a specific capacitance of 193 F g<sup>-1</sup> was obtained using a sort of Mn<sub>3</sub>O<sub>4</sub> films as electrode for supercapacitor and Jiang and Kucernak [19] also reported manganese oxide with a chemical composition of Mn<sub>3</sub>O<sub>4</sub> and containing a moderate amount of carbon use for supercapacitor previously, and a specific capacitance of 145 F g<sup>-1</sup> was obtained. However, the Mn<sub>3</sub>O<sub>4</sub> prepared in the two literature were both in size greater than 5 μm, while the Mn<sub>3</sub>O<sub>4</sub> of aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite in this paper is about 200 nm. The manganese oxide with nano-structure

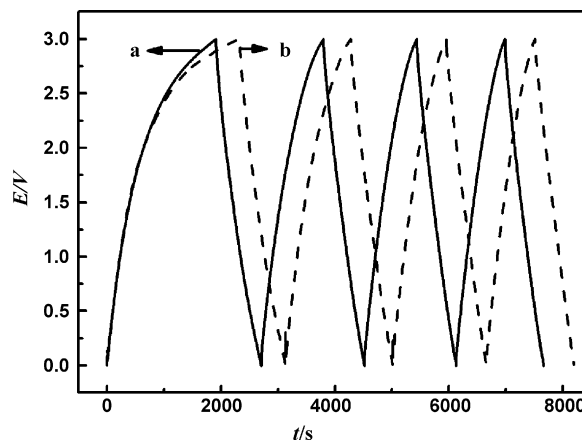


Fig. 4. Charge–discharge curves of (a) aMCMB/Mn<sub>3</sub>O<sub>4</sub> composite electrode and (b) aMCMB electrode at current density of 330 mA g<sup>-1</sup>.

is conducive to increase the utilization of material due to the large surface area [15,20], it is probably the main reason for the high capacitance of the  $\text{Mn}_3\text{O}_4$  in aMCMB/ $\text{Mn}_3\text{O}_4$  composite electrode. It is clear that metal oxides were adsorbed onto activated carbon with good conductivities, provided excellent environment of electrons conduction for metal oxide and improved poor electrical conductivity of metal oxide itself, and the high pseudo-capacitance of metal oxide could be a good offset to the electrical double-layer capacitance of carbon-based materials [15,21,22]. It is most likely that there is a significant improvement in electrochemical properties of aMCMB/ $\text{Mn}_3\text{O}_4$  composite electrode due to the presence of  $\text{Mn}_3\text{O}_4$ . In  $\text{LiPF}_6$  organic electrolyte, the Faraday reaction of  $\text{Mn}_3\text{O}_4$  in charge–discharge process is likely to be based on one redox process in which  $\text{Li}^+$  is inserted and extracted from solution into manganese oxide matrix [23,24]:  $\text{MnO}_x + \delta\text{Li}^+ + \delta\text{e}^- = \text{Li}_\delta\text{MnO}_x$ , and the definite reaction mechanism needs for further study. Consequently, a further work on the pseudo-capacitance mechanism of  $\text{Mn}_3\text{O}_4$  and cycling performance of aMCMB/ $\text{Mn}_3\text{O}_4$  composite electrode in organic electrolytes and improvement to the specific capacitance are important for its potential application in electrochemical supercapacitor.

#### 4. Conclusions

In this study, we report a new type of aMCMB/ $\text{Mn}_3\text{O}_4$  composite electrode for supercapacitors, in  $1 \text{ mol L}^{-1} \text{ LiPF}_6/(\text{EC} + \text{DMC})$  organic electrolyte. The specific capacitance of the electrode is up to  $178 \text{ F g}^{-1}$  at a current density of  $330 \text{ mA g}^{-1}$ . The charge–discharge curve of the aMCMB/ $\text{Mn}_3\text{O}_4$  electrode shows typical capacitive behavior with a good linear slope, and the CV curve also shows good rectangular and symmetric current–potential characteristics of a capacitor. These results demonstrate this aMCMB/ $\text{Mn}_3\text{O}_4$  composite is a good candidate as electrode material for electrochemical capacitor.

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