



Enhanced low temperature performances of expanded commercial mesocarbon microbeads (MCMB) as lithium ion battery anodes

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ABSTRACT

Expanded mesocarbon microbeads (EMCMB) are prepared by oxidizing pristine mesocarbon microbeads (MCMB). The d_{002} value calculated from X-ray diffraction results shows that the average interlayer distance of MCMB increases after oxidizing modification. The increased interlayer distance facilitates Li^+ insertion kinetics, which causes an extraordinarily improved capacity of EMCMB (100 mAh g^{-1}) at -40°C , compared with pristine MCMB (almost no capacity at -40°C). The facilitated Li^+ insertion kinetics is analyzed by electrochemical impedance spectroscopy (EIS). EIS results demonstrate that both charge-transfer resistance and Li^+ diffusion resistance of the EMCMB decrease obviously. The diffusion coefficients of Li^+ in MCMB and EMCMB at -40°C calculated from EIS are $2.46 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ and $1 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, respectively.

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1. Introduction

The low capacity of Li ion batteries at low temperature ($< -20^\circ\text{C}$) has restricted their applications in some special environments, such as high latitude, cold winter and aerospace. When the temperature falls below -20°C , both the power and energy are substantially lost [1–3]. It has been reported that, a commercial 18650 Li ion battery delivers only 5% of energy density at -40°C , compared with the value at 20°C [4]. The main factors affecting low temperature performances can be summarized as follows: reduced conductivity of the electrolyte and the solid electrolyte interphase (SEI) film; increased Li^+ insertion resistance in the electrode materials due to increased activation energy in electrochemical reaction and decreased Li^+ diffusion kinetics at low temperature [2].

The low temperature conductivity of electrolyte can be improved by adjusting the electrolyte components. For example, the electrolyte has a better conductivity when propylene carbonate (PC) replaces ethylene carbonate (EC). On the other hand, adding co-solvents can transfer the SEI components, which may reduce the resistance at low temperature. However, there is a rare report on improving low temperature performances by improving Li^+ insertion kinetics, which is considered to affect the low temperature performance more significantly than the electrolyte

conductivity and the SEI film resistance [2]. In this study, the relationship of Li^+ insertion kinetics in the graphite anode was investigated. Commercial mesocarbon microbeads (MCMB) were modified by oxidation and subsequent heat treatment. The results presented here demonstrate that the low temperature performances of modified MCMB have an excellent improvement compared with pristine MCMB.

2. Experimental

All chemical reagents used in the experiments were analytically pure. Firstly, 3 g MCMB powder, provided by BTR Company (Shenzhen China), was dispersed in 20 ml concentrated H_2SO_4 . Then, 4 g KMnO_4 was added gradually with stirring. The mixture was then stirred at room temperature for 2 h. After that, 30 ml distilled water was added in. Then, the reaction was terminated by the addition of 10 ml H_2O_2 . The mixture was filtered and washed to neutral with deionized water. The obtained powder was dried in a vacuum oven at 50°C overnight. Finally, the above oxidized MCMB were heat-treated at 800°C in Ar atmosphere for 3 h. The modified MCMB were defined as expanded MCMB (EMCMB).

The crystal structures of MCMB and EMCMB powders were identified by powder X-ray diffraction (XRD) on a Rigaku D/max-2000 X-ray diffractometer with monochromated $\text{Cu K}\alpha$ radiation (45 kV, 50 mA). The morphologies of the powders were observed using a scanning electron microscope (SEM, HITACHI, S-4700).

Electrochemical tests were carried out in the CR2025 button testing batteries using a two electrode electrochemical cell

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consisting of a MCMB or EMCMB electrode, two sheets of micro-porous membrane (Celgard 2400) and Li foil as the counter electrode. MCMB or EMCMB electrode areas of 154 mm^2 coated on Cu foil were used for electrochemical measurements (MCMB or EMCMB:polyvinylidene fluoride (PVDF):carbon black=7:2:1, weight ratio). The low temperature electrolyte was provided by Tinci Company (Guangzhou China). A BTS-2000 Newware Battery Testing System was used for charge/discharge testing over a voltage range of 0.01–1.5 V vs. Li^+/Li at 0.2 C ($1 \text{ C}=376 \text{ mAh g}^{-1}$). A CHI 660D electrochemical workstation was employed for the electrochemical impedance spectroscopy (EIS).

3. Results and discussion

The SEM images in Fig. 1c and d demonstrate that the EMCMB have an increase in the normal direction of graphite layers compared with the pristine MCMB (Fig. 1a and b). Although there are obvious crannies between the graphite layers of EMCMB, the graphite layers have not been exfoliated completely like preparing graphene nanosheets [5]. XRD patterns in Fig. 2 show that the degree of graphitization decreases after expansion. The humps that appeared in the patterns of both MCMB and EMCMB at 23° are the characteristic peak of amorphous carbon, which may exist in the pristine MCMB originally. The d_{002} values of MCMB and EMCMB calculated from (002) peaks of the samples are 0.337 nm and 0.351 nm, respectively. The obvious increase of d_{002} value indicates that the MCMB have a larger interlayer distance after expanding modification. However, it is clearly seen that the EMCMB have not lost the graphite structure, which can be verified by the clear patterns (ascribed to JCPDS: 41-1487) of the inset in Fig. 2. The SEM and XRD results reveal that the EMCMB still maintain a graphite structure in spite of the strong

oxidization, which can be attributed to the subsequent re-graphitizing by heat treating.

Discharge/charge curves of Li^+ insertion/extraction into/from MCMB and EMCMB at different temperatures are shown in Fig. 3. The capacity of MCMB still delivers over 130 mAh g^{-1} at -10°C . Then, it decreases to 39 mAh g^{-1} at -30°C , and there is no capacitance at -40°C , as shown in Fig. 3a. However, EMCMB have an insertion capacity of 96 mAh g^{-1} and an extraction capacity of 100 mAh g^{-1} at -40°C (Fig. 3b), which are much higher than that of MCMB at -40°C .

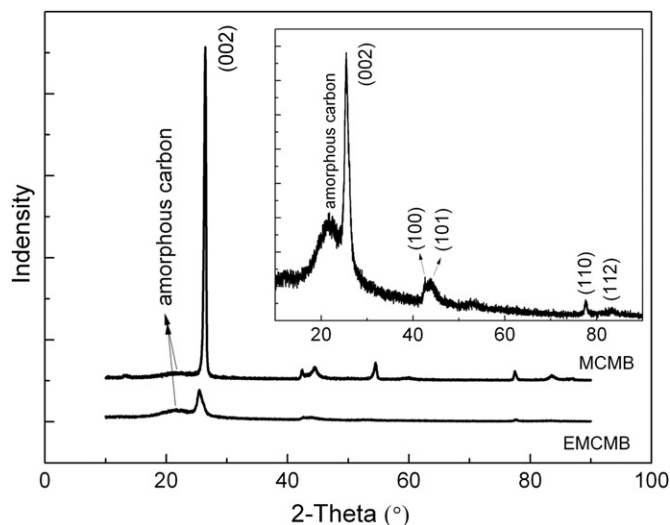


Fig. 2. XRD patterns of MCMB and EMCMB, inset is the clear XRD patterns of EMCMB.

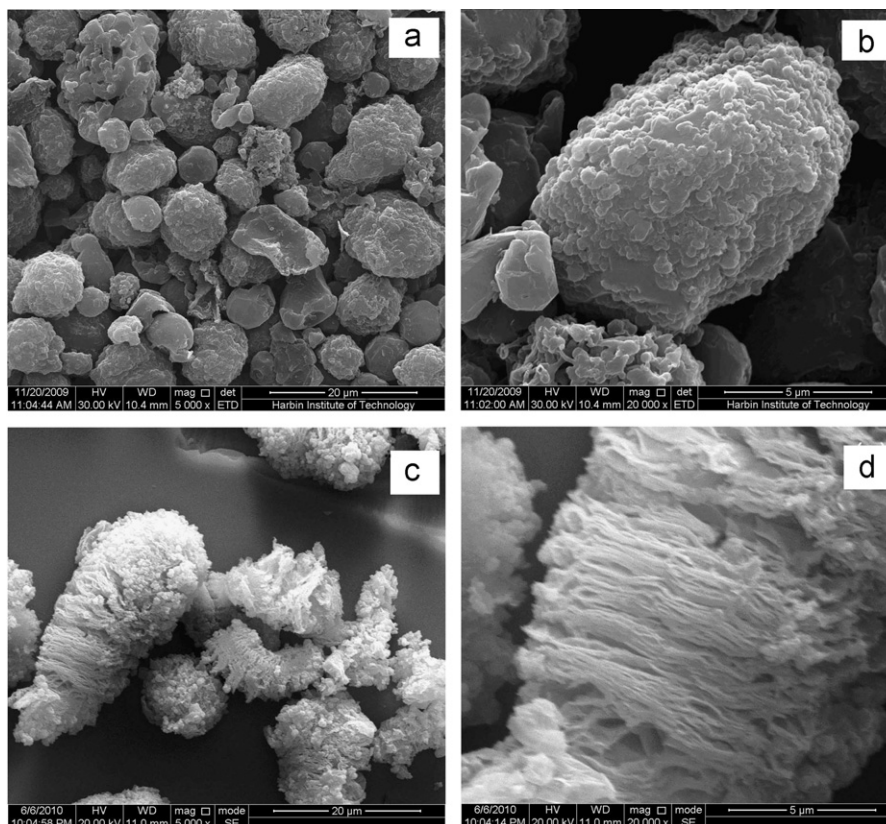


Fig. 1. SEM images of MCMB (a,b) and EMCMB (c,d).

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