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Porous graphite prepared by molybdenum oxide catalyzed gasification as anode material for lithium ion batteries

Tianshu Deng [a,b], Xiaoping Zhou [a,*]

[a] Department of Chemical Engineering, Hunan University, Changsha, Hunan 410082, PR China
[b] Microvast Inc., PR China

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ABSTRACT

Porous graphite was successfully prepared by MoO_x-catalyzed gasification. The prepared graphite with pores and channels exhibits an excellent cycling stability at high rate as anode materials for Lithium ion batteries. The porous graphite offers better cycling performance than the pristine graphite, retaining 84% of its initial reversible capacity after 1500 cycles at rate 5C. The effective synthesis strategy might open new avenues for the design of high-performance graphite materials.

1. Introduction

Lithium ion batteries (LIBs) are widely used for portable electronic devices, and they are also being intensively pursued for applications in electric and hybrid vehicles [1,2]. In vehicle applications, the charging rate of the LIB is the most important characteristic for practical use because it is not feasible for electric vehicle (EV) users to wait for more than 2 h to charge their vehicles (it generally takes 2–6 h to charge the EV with graphite anode).

Presently, graphite has been the most commonly used LIB anode material owing to its high energy density and low cost [3]. However, the narrow inter layer spaces (0.335 nm) and the long diffusion distance of lithium ions in graphite crystals result in high lithium ion diffusion resistance. A high charging rate can lead to the fatal growth of dendrites on the metallic lithium plating on the graphite surface [4]. Various strategies of modification methods were applied in graphite preparation, i.e. the surface oxidation [5], the surface fluorination [6], the metal coating [7], and the carbon coating [8]. These modifications could usually reduce the surface active species, and reduce the initial irreversible capacity of batteries. However, these modifications could not improve the lithium diffusion rate in graphite particles. Because lithium ions intercalate-deintercalate from the edges of graphite layers, preparation of porous graphite through the formation of pores and channels in graphite crystals may be an effective approach to improve the lithium diffusion rate.

Catalytic gasification of graphite in oxygen [9], carbon dioxide [10], hydrogen [11], and steam [12] by various metals and metal oxide catalysts has been well studied. Yet to the best of our knowledge, there have been no reports of these porous graphite materials for use in forming anode materials for lithium-ion batteries through hot steam catalyzed gasification process. In this work, we prepared porous graphite by MoO_x-catalyzed gasification of graphite. Lithium ions can be intercalated into the graphite crystals through the pores and channels; additionally, the pores and channels could buffer the volume change of graphite in the charging-discharging cycles, so the porous graphite exhibit good electrochemical performance.

2. Experimental section

Synthesis of porous graphite: Commercial graphite (GHMG-M G0812, 1500 g, Chuang Ya Inc.) was added into a $H_{24}Mo_7N_6O_{24}$ solution (3500 g, containing 8.85 g of $H_{24}Mo_7N_6O_{24}$) under agitation for 1 h, and the solution was then dried in a spray dryer (180 °C) to obtain a powder sample. The powder sample (400.0 g) was placed into a tube furnace under N_2 (100 ml/min). The furnace was heated to 900 °C at a ramp rate of 5 °C/min. After the temperature was stabilized at 900 °C, liquid water was pumped into

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[*] Corresponding author.
E-mail addresses: tianshudeng@163.com (T. Deng), hgx2002@hnu.edu.cn (X. Zhou).

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the tube furnace at the rate of 0.20 ml/min. After reacting for 15 h, the furnace was cooled to room temperature in N_2 to obtain the porous graphite (GMo). Details of the material characterization and electrochemical measurements are described in the Supplementary data.

3. Results and discussion

The SEM images in Fig. 1 show the morphologies of the graphite samples before and after the steam gasification. The pristine graphite shows a smooth surface (Fig. 1a). After the graphite was subjected to catalytic steam gasification, a large number of pores and channels could be seen in GMo (Fig. 1b).

The data in Table 1 show that following the reaction of the Mo loaded graphite with steam at 900 °C for 15 h, the graphite lost 12.1% of its weight, and the specific surface area of graphite increased from 1.9 m^2/g to 10.1 m^2/g. The tap density of graphite was reduced from 0.98 g/ml to 0.89 g/ml. These results indicate that pores and channels have been created in the graphite crystals.

The X-ray diffraction patterns of the pristine graphite and the GMo are shown in Fig. 2a. It is found that the GMo has a strong diffraction peak at 26.5°(002) with the d_{002} (d_{002} stands for the distance between any two closest crystal facets) equal to 3.36 Å, which is close to that d_{002} values (3.35 Å) of the pristine graphite. This result indicates that the GMo has the same lattice structure as that of the pristine graphite. Hence, the graphite lattice structure is still retained in GMo. Fig. 2b shows the Raman spectra of the pristine graphite and the GMo. Higher ID/IG (intensity of D band/ intensity of G band) ratios correspond to graphite with more edges, defects, and disorder in its lattice [13]. In the present investigation, the ID/IG ratio of GMo is 0.35, while that of pristine graphite is 0.13. The obtained results indicate that edges, defects, and disorder are well-developed in GMo.

Fig. 3a shows the initial charge and discharge curves of the half cells prepared from the pristine graphite and GMo. The results show that GMo has higher specific capacity than pristine graphite. The reason could be that the GMo could accommodate more lithium ions in the nano-pores of GMo material [14]. However, GMo has relatively lower initial columbic efficiency than the pristine graphite. This could be due to the existence of larger number of edges, defects, and disordered features in GMo, leading to more irreversible lithiation of the anode. However, in the following charging-discharging cycles, almost 100% of columbic efficiency was reached.

Examination of the curves in Fig. 3a shows that the discharge voltage of the GMo cell is higher than that of the pristine graphite cell, and the charge voltage of the GMo cell is lower than that of the pristine graphite cell. These results indicate that the GMo cell has a lower lithium ion diffusion resistance than the pristine cell. This may be due to the pores in the GMo offering extra pathways for lithium ions intercalation into the graphite crystals.

Table 1
Characterizations of pristine graphite and GMo.

	Weight loss (%)	Specific surface area (m^2/g)	Tap density (g/ml)
Pristine graphite		1.9	0.98
GMo	12.1	10.1	0.89

The cycling performances of the scaled-up batteries (designed as 3 Ah) are shown in Fig. 3b and d. The results show that the cycling stability of the GMo batteries is better than that of the pristine graphite battery (PGB), especially at high rate charging-discharging cases. For instance, when the charging rate is raised to 5C (Fig. 3c), the PGB fully degrades within 300 cycles; by contrast, the GMo battery still retains 84% of its original capacity at its 1500th cycle. The results indicate that a high charging rate leads to fatal damage to the PGB. Fig.3d shows that the GMo batteries have almost the same good cycling stability when they are charged at 1C, 3C, and 5C and 6C. These results indicate that the batteries with porous graphite anodes are much more stable than that those with the pristine graphite anodes, especially when the batteries are charged at a high rate.

When checking the data of Fig.3d more carefully, we can see the high rate charging-discharging batteries perform better than low rate charging-discharging batteries. The reason is that with the same cycle number, the high rate charging batteries work shorter time at high temperature (45 °C) in the oven than the low rate charging batteries (the oven temperature was kept at 45 °C). Hence, the long working time at high temperature is the major reason that leads to battery degradation.

It is known that the diffusion time of lithium ions in solid graphite is proportional to the square of the diffusion length (L) ($t \approx L^2/D$) (D is the lithium ion diffusion coefficient) [15,16]. In the porous graphite, many pathways could be filled in by the electrolyte solution and the diffusion distance of lithium ions in the graphite lattice was greatly shortened. Hence, the existence of the pores and channels in graphite particles reduced the diffusion distances and the resistance of lithium ions. In addition to the favourable diffusion kinetics in graphite particles, the pores and channels in graphite could also act as buffers for volume change (because graphite exhibits a volume change of approximately 10% during the battery charging-discharging cycle. [17]). Hence, the

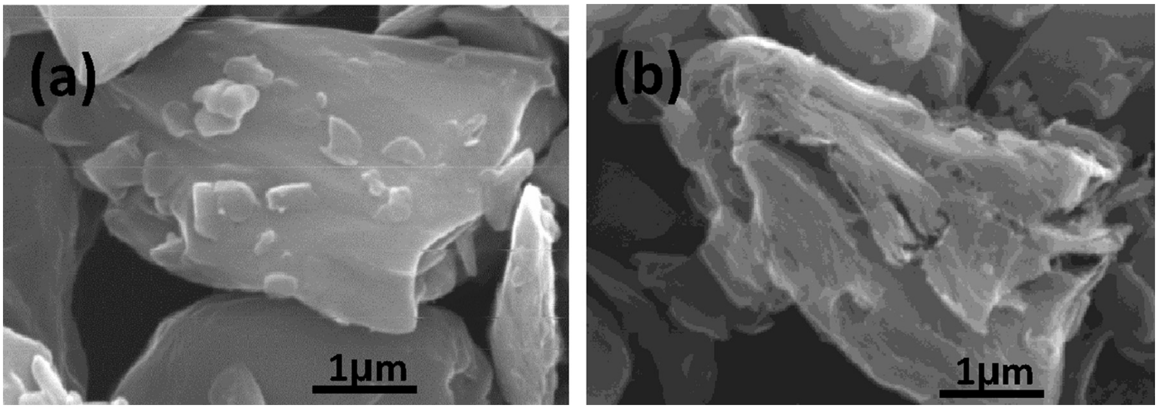

Fig. 1. SEM images of (a) pristine graphite and (b) GMo.