



Commercial expanded graphite as a low-cost, long-cycling life anode for potassium-ion batteries with conventional carbonate electrolyte



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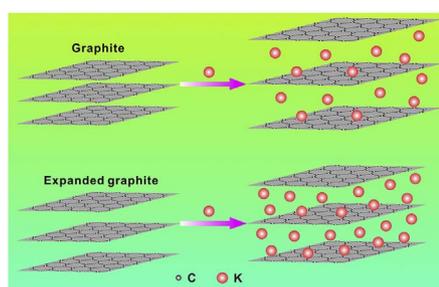
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HIGHLIGHTS

- Expanded graphite is used as anode for potassium-ion battery for the first time.
- The expanded graphite showed excellent electrochemical performance.
- The potassium storage mechanism of expanded graphite is investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Design and synthesis of capable anode materials that can store the large size K^+ is the key of development for potassium-ion batteries. The low-cost and commercial expanded graphite with large particles is a graphite-derived material with good conductivity and enlarged interlayer spaces to boost the potassium ion diffusion coefficient during charge/discharge process. Thus, we achieve excellent anode performance for potassium-ion batteries based on an expanded graphite. It can deliver a capacity of 263 mAh g^{-1} at the rate of 10 mA g^{-1} and the reversible capacity remains almost unchanged after 500 cycles at a high rate of 200 mA g^{-1} with a coulombic efficiency of around 100%. The potassium storage mechanism is investigated by the ex situ XRD technique. This excellent potassium storage performance will make the expanded graphite promising anode candidate for potassium ion batteries.

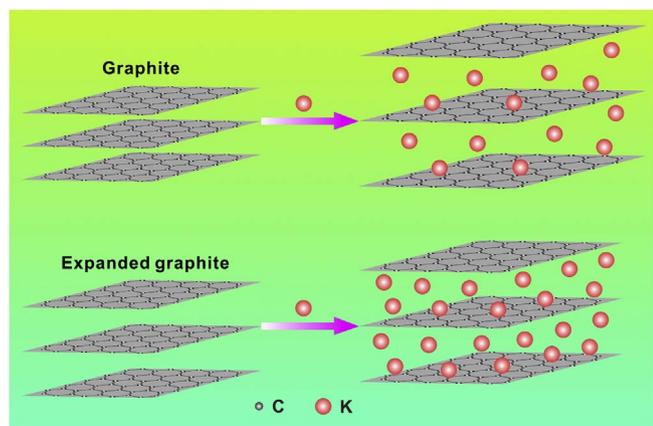
1. Introduction

With the development of portable electronic devices and electrical vehicles, there is a crucial demand for new and sustainable battery systems of high energy density [1]. Lithium-ion batteries (LIBs) have been actively developed due to their high energy density [2]. However, owing to the lithium scarcity, its uneven global distribution and increasing cost, the widespread large-scale application of LIBs has been limited [3]. Therefore, there is an urgent need for an alternative battery

system based on the earth-abundant elements [4]. Sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) have attracted great attention to obtain economically rechargeable battery systems due to the abundance and low-cost of sodium and potassium elements [5]. In contrast to 0.0017 wt% of lithium element in the earth's crust, the potassium element is the seventh most abundant, the content of which is close to the sodium element (2.09 wt% vs. 2.36 wt%) [6]. More importantly, close to the redox couple of Li/Li^+ (-3.04 V), the redox potential of K/K^+ (-2.93 V) is lower than that of sodium counterpart

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Scheme 1. Schematic illustration of potassium storage in graphite and expanded graphite.

(−2.71 V) [7]. Thus, the PIBs have a higher working voltage and energy than SIBs [8,9]. Komaba et al. proved that the PIBs may be the promising capable of being 4 V class battery systems [10]. Therefore, the PIBs of low cost can be expected and will be prospective [11,12]. (see Scheme 1).

Materials that have been introduced for electrodes for PIBs are quite limited [13]. For the cathode side, layered oxides, Prussian blue analogues, and organic solids or polymers [14–18]. As for the anode side, several carbon-based materials have been investigated for PIBs in previous studies [19–21]. Ji et al. proved a three-stage process of K^+ insertion into graphite ($C \rightarrow KC_{36} \rightarrow KC_{24} \rightarrow KC_8$) and found out that the high rate capability of graphite anode is unfavourable in the nonaqueous electrolyte, thus they presented a soft carbon as the high rate anode material with a theoretical capacity of 273 mAh g^{-1} for the PIBs [19]. Owing to the lowest voltage and feeblest solvation among lithium, sodium, potassium, magnesium, calcium ion carriers, the potassium shuttlecock mechanism between two intercalation materials as PIBs is propitious for higher-power/voltage rechargeable batteries [10]. Furthermore, Ji and his co-workers also studied the hard carbon microspheres as the anode material that exhibited a high initial capacity of 262 mAh g^{-1} with a capacity retention of 83% after 100 cycles in PIBs [20]. Compared to the rate performance in SIBs, the hard carbon microspheres displayed a much better high rate property in PIBs, which may be attributed to the higher diffusion coefficient of K^+ in the special structure compared to Na^+ [20]. These carbon-based materials have indicated their great potential as anode materials for PIBs. However, among all carbon-based materials, the low-cost graphite, which is a commercial electrode material for LIBs, exhibits limited electrochemical performance when it is used as the anode for PIBs [9]. Owing to its long diffusion pathways (several micrometers) and the narrow interlayer spaces (0.34 nm), the high ion diffusion resistance of graphite is a major barrier to the incorporation of the K^+ into a metal-carbon complex substance with the stoichiometry of KC_8 , which directly impacts its rate property [19,20]. In addition, the K^+ is more difficult to insert graphite than Li^+ due to the ionic radii that the K^+ ion is greater than Li^+ ion, which also contributes to the lower rate capability of graphite anode in PIBs [9–12].

Hence, we report the expanded graphite (EG) as a superior PIBs anode material to promote the application of commercial and low-cost available graphite in PIBs with improved electrochemical performance in this work. EG is a graphite-derived material with good conductivity and enlarged interlayer spaces to boost the ion diffusion coefficient during charge/discharge process. Thus, we achieved excellent anode performance for potassium-ion batteries based on an expanded graphite, which can deliver a capacity of 263 mAh g^{-1} at the rate of 10 mA g^{-1} and the reversible capacity remains almost unchanged after 500 cycles at a high rate of 200 mA g^{-1} with a coulombic efficiency of

around 100%. The potassium storage mechanism is investigated by the ex situ XRD technique. This excellent potassium storage performance will make the expanded graphite promising anode candidate for potassium ion batteries.

2. Experimental

2.1. Materials

Expanded graphite (EG) and commercial graphite (CG) were purchased from Shandong Guyu Co (China). The metallic potassium (K, 99.9%) was purchased from Aladdin Industrial Corporation. The polypropylene separator (Celgard 2400), acetylene black, N-methyl-2-pyrrolidone (NMP) and polyvinylidene fluoride (PVDF) were obtained by Shenzhen Kejingstar Technology Ltd. The components of the electrolyte, including potassium bis-fluorosulfonyl imide (KFSI, 99.98%), diethyl carbonate (DEC, 99.95%) and ethylene carbonate (EC, 99.95%), were provided from Dodochem. The electrolyte for the PIBs was home-made with the composition of 1 M KFSI in EC/DEC (1:1, v/v). All the chemicals were applied directly without further purification.

2.2. Characterization methods

Crystallographic phases were collected by X-ray diffraction (XRD) on a Rigaku Dmaxrc diffractometer using $Cu \text{ K}\alpha$ radiation (35 kV, 20 mA, $\lambda = 1.5418 \text{ \AA}$) at a scanning rate of $10^\circ \text{ min}^{-1}$ from 10° to 90° . The microstructure of the CG and EG was investigated by a Raman system with an excitation wavelength of 532 nm. The morphology and size of the samples were measured using the SU-70 scanning electron microscopy (FESEM) and the JEOL JEM-2100 high resolution transmission electron microscopy (HRTEM). The porous performance based on the nitrogen adsorption-desorption isotherms was measured by Brunauer-Emmett-Teller theory (BET, ASAP 2020).

2.3. Electrochemical measurements

The slurry was arranged by mixing 80% EG, 10 wt% Super P carbon, 10 wt% sodium carboxymethylcellulose (CMC) binder, 80% CG, 10 wt% Super P carbon, 10 wt% sodium carboxymethylcellulose (CMC) binder, respectively. Then the obtained slurry was pasted onto a Cu foil using a current collector. After drying at 80° C for 24 h in a vacuum oven, the electrodes were cut into small rounds with a diameter of 14 mm. The mass loading of active materials was about 2 mg cm^{-2} . Compared to commercial graphite anode, the mass loading in our experiment is lower, one reason is that the weight ratio of binder and conductive agent is much higher (20%) than commercial level (less than 10%), which reduces the mass loading; The other reason is that the density of expanded graphite is lower than graphite. More work may be done to optimize the fabrication process and the morphology (such as spherical). The potassium metal was applied as the counter electrode and reference electrode. Glassy-fiber was used as the separator. The electrolyte was 1 M KFSI in diethyl carbonate/ethylene carbonate (DEC/EC, v/v = 1:1). All the cells were installed in a glovebox filled with argon and measured in a room temperature. The electrochemical performance was tested by a galvanostatic programmable battery charger in a 2016 cell with voltage range of 0.01 V–3 V (vs. K/K^+). Cyclic voltammetry (CV) was checked out between 0.01 V and 3 V at scanning rate of 0.1 mV s^{-1} with an electrochemical workstation. Ex situ XRD measurements were carried at different statuses during the first charge-discharge cycle. The electrode was washed with DEC to remove the residual electrolyte and then dried at 60° C for 10 h before being tested.

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