



# KOH etched graphite for fast chargeable lithium-ion batteries



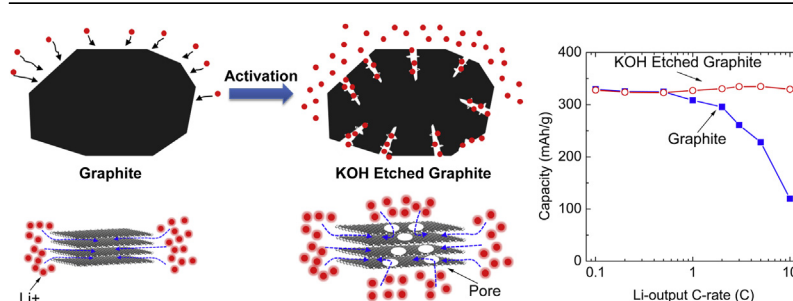
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## HIGHLIGHTS

- KOH etched graphite is proposed for fast chargeable lithium ion batteries anode.
- A KOH method is used to etch the surface of graphite material.
- The KOH etched graphite has a lower specific capacity and higher coulombic efficiency.
- KOH etched graphite anode shows better charging and discharging rate capability and cyclability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Graphite is the most widely used anode material for lithium ion (Li-ion) batteries, although it has limited power performance at high charging rates (Li-ion input). Alternative materials such as silicon and tin alloys, however, have an even more inferior rate capability. We describe here a multi-channel structure with a graphite surface etched with pores that can greatly increase the number of sites for Li-ion intercalation/de-intercalation and reduce the Li-ion diffusion distance for fast chargeable Li-ion batteries by etching the graphite surface with pores. As a result, the multi-channel structure graphite anode shows better charging and discharging rate capability, cyclability, and higher coulombic efficiency than pristine graphite materials. The multi-channel anode material is proposed for use in fast chargeable Li-ion batteries for electric vehicles and plug-in hybrid vehicles.

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## 1. Introduction

Lithium-ion (Li-ion) batteries have been widely used for portable electronics, and they are being intensively pursued for hybrid vehicles (HVs), plug-in hybrid vehicles (PHVs), electric vehicles (EVs), and stationary power source applications for smarter energy management systems. The greatest challenges in adopting the technology for large-scale applications are the energy density, power density, cost, safety, and cycle life of current electrode

materials. Of all the properties, the charging time as well as the power density is the most important characteristics for the battery, especially as the application targets of Li-ion batteries move from small mobile devices to transportation. This is because EV users, for example, are hardly to wait more than half an hour to charge their vehicles during a long drive compared with a refueling period of less than 5 min for gasoline cars. The speed of charge greatly depends on the lithiation rate capability of anode materials.

At present, graphite is the most popular and practical anode material for Li-ion batteries because of its low cost, high capacity, relatively long cycle life, and ease of processing [1–4]. However, the small interlayer spaces (0.335 nm), the lack of Li-ion intercalation sites on the natural graphite basal plane, and the long diffusion

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range among the graphite interlayers result in a limited lithiation rate capability of graphite anode materials (Fig. 1a) [5–7]. Amorphous carbon such as soft carbon and hard carbon usually have larger interlayer spaces than graphite, offering a faster lithium input rate than graphite [8–11]. However, because soft carbon usually has a limited capacity (around 250 mAh/g) and higher average potential while charging and discharging, it is difficult to use it in Li-ion batteries with high energy density. Hard carbon has a capacity around 400 mAh/g, but its low density, low coulombic efficiency, and high cost make it difficult to use in batteries for EVs and PHVs at a low enough cost. Other high capacity anode materials such as silicon and tin alloys have even worse lithiation rate capabilities because of the low kinetics of lithium alloying and the accessibility of lithium ion through thick SEI [12,13]. As a result, graphite is still considered to be the most promising anode material in a practical sense.

Chemical activation with alkali compounds such as KOH and NaOH is a well-known method to activate carbon materials with a high surface area up to 3000 m<sup>2</sup>/g [14–17]. Activated carbon with a specific high surface area has many applications such as in electrochemical double-layer capacitors. However, it is quite harmful if a graphite anode has a high specific surface area because it results in low initial charge/discharge coulombic efficiency and a poor cycle life. Moreover, some cathode materials, such as LiMn<sub>2</sub>O<sub>4</sub> which can also be synthesized by templates or other methods to form a porous structure for better rate capability and cycle life [18–20]. In this study, a multi-channel structure was proposed as a way to increase the number of Li-ion intercalation sites and reduce the Li-ion diffusion distance among the interlayers while charging and discharging by etching holes in the surface of pristine graphite without increasing the specific surface area by using a KOH etching method. The multichannel structure is showed schematically in Fig. 1b.

## 2. Experimental section

### 2.1. Synthesis of multi-channel graphite

The KOH etched graphite was synthesized from granulated natural graphite by using a KOH etching method, as shown in Fig. 2 [21]. We used 10 g of granulated natural graphite (CGB-20, Nippon Carbon Industries, Ltd) with a particle size of 20 μm and mixed it with 500 ml of 7 M aqueous KOH solution. This was stirred for 12 h at a speed of 300 rpm in ambient conditions. The extra KOH solution was removed by vacuum filtration of the mixture through a PTFE (polytetrafluoroethylene) membrane (Whatman, 1 μm); then the mixture was dried in vacuum at 80 °C for 12 h. The dried KOH with attached graphite powder was heat treated at 800 °C for 1 h in a nitrogen gas flow oven at the speed of 5L/min. The

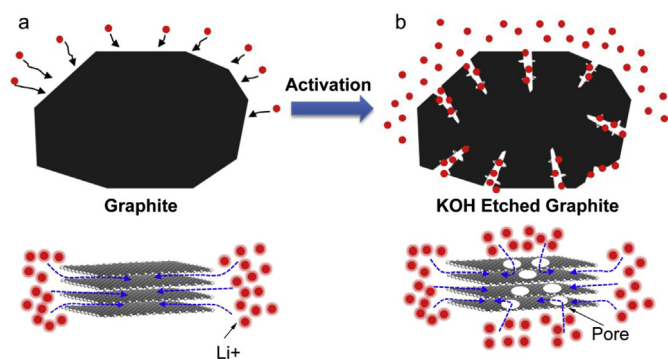


Fig. 1. Schematic scheme of a) pristine graphite and b) KOH etched graphite.

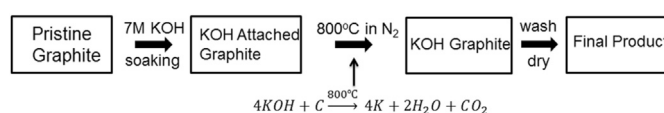


Fig. 2. KOH graphite fabrication process.

temperature was increased from the room temperature to 200 °C at 1 °C/min and kept at 200 °C for 30 min. Then the temperature was increased to 800 °C in 1 h. After the heat treatment, the black powder was washed with distilled water several times to remove the residual KOH, and the final product was collected by vacuum filtration and dried in a vacuum oven.

### 2.2. Characterization

The morphology of the products was examined by using field-emission scanning electron microscopy (FE-SEM) (Hitachi, SU8000). The particle distribution was analyzed with a particle analyzer (Shimadzu, SALD-2200). Fourier transform infrared (FT-IR) spectra of the samples were recorded by an FT-IR spectrophotometer (Bruker Optics) using the KBr method. Raman spectroscopy was performed using an NRS-7000 series device with a maximum resolution of 0.7 cm<sup>-1</sup>/0.3 cm<sup>-1</sup> and a measurement range from 50 to 8000 cm<sup>-1</sup>. A two-electrode cell configuration in a laminate cell was used to measure the performance of rate capability. The cut potential range for the half-cell measurement was from 0 V to 1.5 V, while the full cell charge and discharge was carried out in the voltage range of 2.3V–4.3 V.

### 2.3. Cell fabrication

The negative electrode was prepared by coating a mixture of granulated natural graphite as the pristine graphite or KOH etched graphite, with a carbon conductive additive, a water-based binder carboxymethyl cellulose, and styrene-butadiene rubber with a weight ratio of 96%: 1%: 1%: 2% on a copper film with a mass loading of 50 g/m<sup>2</sup>. The density of both the pristine graphite and the KOH etched graphite was controlled to 1.5 g/cm<sup>3</sup>. The electrolyte used was 1 M LiPF<sub>6</sub> EC/DEC (3:7).

## 3. Results and discussion

### 3.1. Characterization of the materials

The morphologies of the carbon materials are shown in Fig. 3. Fig. 3a is the pristine graphite material, from which the smooth surface is revealed. The diameter of the granulated natural graphite is around 15–20 μm. Fig. 3b shows an SEM image after KOH nano-crystal deposition. The enlarged surface morphology is shown in the inset of Fig. 3b. KOH nano-crystals 10–100 nm in size are attached to the surface of the graphite. The particles after heat treatment are shown in Fig. 3c. Holes with a size of around 1–2 μm can be seen and are marked by white circles. The 1–2 μm holes are larger than the KOH crystals because the KOH crystals melted and aggregated into a larger size during the heat treatment to 800 °C. Different from the solution and gases activation methods, graphite can be etched in both edge and basal plane by this method. The particle size distribution before and after the KOH etching is shown in Fig. 4. There is almost no change in the distribution between the two samples, which means the KOH etching does not reduce the size of the graphite particles.

Nitrogen adsorption and mercury intrusion methods were used to characterize the pore distribution before and after the KOH

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