



## Increasing reversible capacity of soft carbon anode by phosphoric acid treatment



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### ABSTRACT

Soft carbon with a high reversible capacity has been proposed as an anode material for high-power lithium ion batteries. In this work, we investigate the effect of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) addition during preparation on the microstructure and electrochemical performance of soft carbon.  $\text{H}_3\text{PO}_4$  facilitates the formation of nanopores by terminating C-C bonding and forming C-O<sub>x</sub>-P ( $0 < x \leq 4$ ) chemical bonds. The newly integrated nanopores are mainly responsible for increasing the reversible capacity of soft carbon and maintaining excellent cycle performance and rate capability. In addition, the proposed synthetic route is simple and cost-effective, which will be helpful for successfully employing soft carbon on a commercial scale.

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### 1. Introduction

Carbonaceous materials have attracted much attention as anode materials for lithium ion batteries (LIBs) since they were first commercialized in 1991. Carbonaceous materials can generally be classified into three types according to their microstructures: graphite, soft carbon, and hard carbon [1,2]. Among these types, graphite has been most widely used in current LIBs because of its high theoretical capacity ( $372 \text{ mAh g}^{-1}$ ), high initial coulombic efficiency ( $\sim 95\%$ ), and excellent reversibility. Despite these attractive features, the poor cycle performance and rate capability of graphite still need to be resolved. As an alternative, soft carbon has been proposed for use in high-power LIBs. Even though soft carbon offers a smaller reversible capacity ( $\sim 300 \text{ mAh g}^{-1}$ ) than graphite, it shows excellent cycle performance and capacity retention even at high current densities. Such promising power characteristics mainly originate from its distinctive microstructure, in which short-range-ordered graphite is randomly arranged in a disordered carbon matrix. This structure is completely different from that of graphite, which has a

well-developed layered structure and amorphous hard carbon structures [3–5].

Soft carbon is generally synthesized by pyrolysis of coke or pitch precursors at a temperature range between 700 and 1800 °C. It is widely recognized that the microstructure of soft carbon is determined by the synthesis temperature and directly affects its electrochemical performance. In particular, the reversible capacity of soft carbon decreases with increasing synthetic temperature, and soft carbon synthesized at temperatures below 800 °C exhibits a higher reversible capacity than graphite [6–8]. However, its low initial coulombic efficiency associated with its poor reversibility hinders its practical use for commercial applications. To overcome those limitations, many studies have focused on tailoring the microstructure of soft carbon in order to control its electrochemical performance.

To improve the reversible capacity of soft carbon, various structural modifications have been proposed. Incorporation of heteroatoms such as B [9,10], N [11,12], Si [13,14], and P [15,16] is effective in increasing the reversible capacity of soft carbon without causing significant performance fading. The incorporated heteroatoms produce more reversible  $\text{Li}^+$  storage sites by forming chemical bonds to C atoms in the structure, which directly contributes to the improved reversibility for  $\text{Li}^+$  insertion and extraction. However, most current approaches for the heteroatom incorporation are based on expensive and/or toxic process such as

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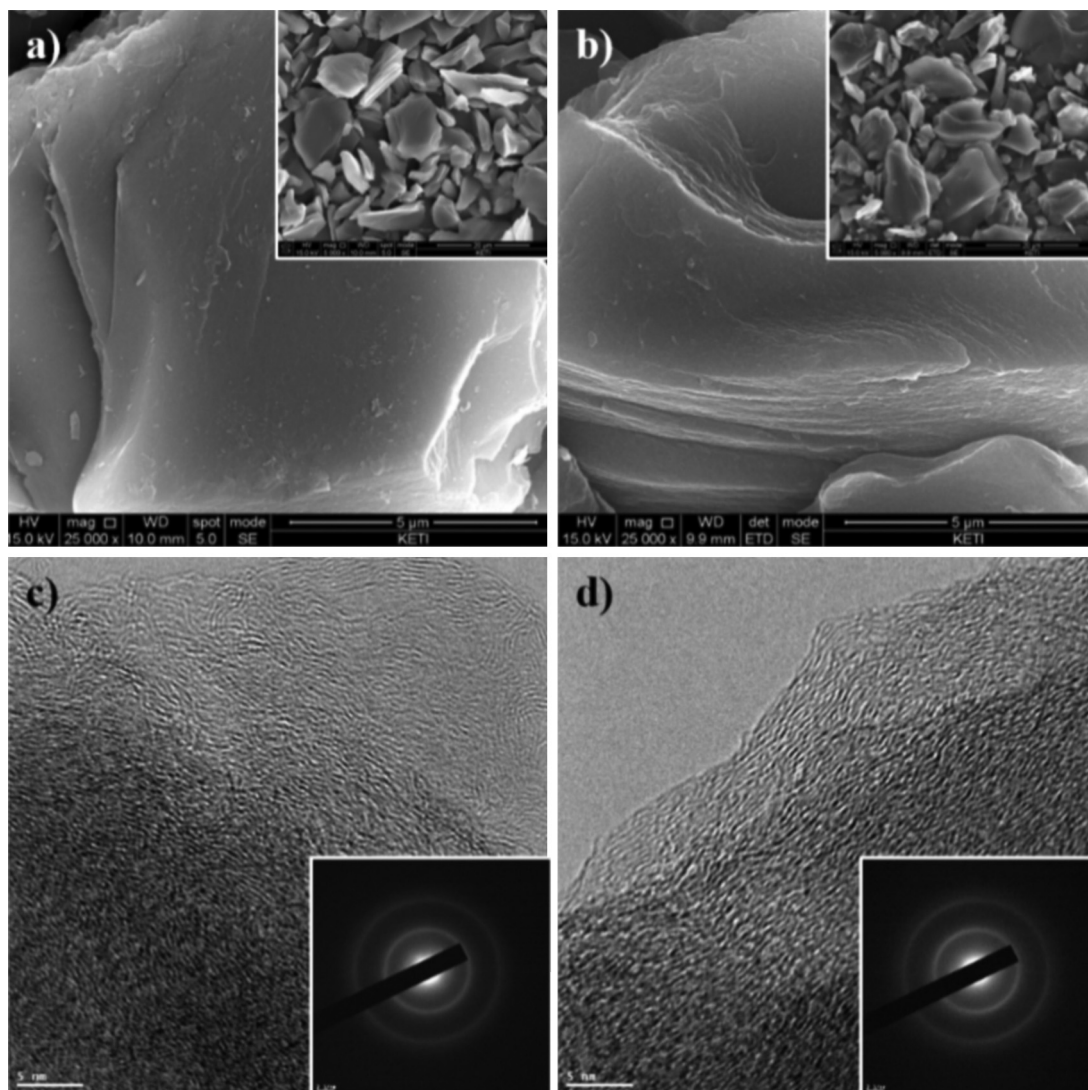
chemical vapor deposition (CVD) or chemical etching [9,11,13]. Thus, there is a strong need for the development of efficient and cost-effective synthetic routes for mass production.

Herein, we introduce a simple method for preparing structurally modified soft carbon by adding phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The correlation between the microstructure and electrochemical properties of the soft carbon is thoroughly investigated based on various structural and electrochemical characterizations. The presented evidence indicates that abundant nanopores can be effectively formed by thermal decomposition of  $\text{H}_3\text{PO}_4$  in the soft carbon, which is essential for improving the reversible  $\text{Li}^+$  storage capacity. Furthermore, the proposed approach is based on a simple and cost-effective process and will be helpful for the employment of soft carbon on a commercial scale.

## 2. Experimental

Pristine soft carbon was prepared by heating petroleum coke precursor at  $900^\circ\text{C}$  for 2 h under Ar flow with a heating rate of  $10^\circ\text{C min}^{-1}$ . From the elemental analysis, we confirmed that as-received petroleum coke precursor has a C/H ratio of 3.96

(atomic). To synthesize  $\text{H}_3\text{PO}_4$ -treated soft carbon, the petroleum coke and 2 wt% (vs. coke mass) of  $\text{H}_3\text{PO}_4$  (85% in water, Aldrich) were thoroughly mixed using a homogenizer (SMT Co., Ltd. HF93), and then heated in a furnace under the same conditions. Elemental analysis for as-received petroleum coke precursor was carried out using an elemental combustion system (Costech Instruments ECS-4010). The surface morphologies and microstructures of the as-prepared soft carbon samples were examined by using a focused ion beam environmental scanning electron microscope (FIB-SEM, FEI Quanta 3D FEG) and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F) with a probe  $\text{C}_s$  aberration corrector (CEOS GmbH). The focused ion beam (FIB, FEI Quanta 3DFEG) was also used for the preparation of cross-sectional specimens for the HRTEM observation. The microstructures of the soft carbon samples were further characterized by Raman spectrometer (Bruker Senterra), X-ray diffraction (XRD, PANalytical Empyrean) with  $\text{Cu K}\alpha$  as the X-ray source and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Sigma Probe).  $^7\text{Li-NMR}$  (Bruker, AVANCE III HD) analysis was carried out for lithiated soft carbon samples at a spin rate of 7 kHz. To prevent contamination of the sample with air or moisture, samples were prepared in an Ar-filled glove box. In addition, the particle size was



**Fig. 1.** FIB-ESEM images for (a) pristine and (b)  $\text{H}_3\text{PO}_4$ -treated soft carbon, and the inset images show the powder shape measured at lower magnification ( $\times 5,000$ ). And HRTEM images for (c) pristine and (d)  $\text{H}_3\text{PO}_4$ -treated soft carbon. The inset images show the SAED of the soft carbon samples.

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