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In situ synchrotron wide-angle X-ray scattering study on rapid lithiation of graphite anode via direct contact method for Li-ion capacitors

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HIGHLIGHTS

- Phase transformation of graphite was characterized by in situ X-ray scattering.
- Direct contact between graphite and lithium metal leads fast lithiation.
- The direct contact method is a robust pre-doping process without any safety issues.
- The study provides an alternative pre-doping method for Li-ion capacitors.

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ABSTRACT

Lithium pre-doping of graphite anode is a key process to achieve high energy density lithium-ion capacitor. In this study, in situ synchrotron wide-angle X-ray scattering examinations directly revealed that the direct contact (DC) method, simply achieved through direct physical contact between graphite electrode and sacrificial lithium metal in electrolyte, provides much faster phase transformation from stage 1′ to stage 1 than conventional electronic charger (EC) and external short circuit (ESC) methods at the same doping time level. The observations indicate that DC method achieves faster pre-lithiation rate of graphite electrode than EC and ESC processes.

1. Introduction

Electrochemical capacitors, also known as supercapacitors, are promising candidates for energy storage technologies with fast charging-discharging rates, high levels of electrical power, and long operating lifetime [1–5]. However, their low energy density compared with the conventional Li-ion batteries (LIB) has limited its energy storage and harvesting applications [6–8]. Recently, Li-ion capacitors (LICs) have attracted considerable interest due to their high energy density compared to conventional electric double layer capacitors (EDLC) [2,9].

The LICs were typically composed of a pre-lithiated negative graphite anode of the LIB and an activated carbon (AC) cathode of the EDLC that were inducing the energy and power density in a range between those of LIB and EDLC [9–11]. The electrochemical performance of the LIC depends on a number of factors, including lithiation degree of graphite anode, types of active materials and electrolytes, and configuration of the electrodes [12–18]. The lithiation, which is called a pre-doping of graphite anode, is a critical process to achieve high performance of LIC devices with long-life cycle operation, because the pre-lithiated graphite anode is capable of maintaining low potential voltage of anode near to the

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potential of pure Li metal during charge/discharge and inducing high operational voltage as well as high energy density [19–22].

Conventional pre-lithiation processes are carried out via EC or ESC method, as shown in Fig. S1. In the EC pre-doping method, graphite electrode and sacrificial lithium metal are separated with a separator in electrolyte and the pre-lithiation of graphite is performed using an electronic charger with an option of constant current or constant voltage [21,23,24]. In the ESC method, graphite and lithium electrodes are separated with a separator in electrolyte, and the pre-doping is spontaneously performed through the external electric wire connection between the two electrodes [25]. However, these approaches need a long pre-lithiation time (mostly much longer than 10 h) for the sufficient pre-lithiation, increasing the total processing cost.

We recently reported that direct contact (DC) between the graphite electrode and sacrificial Li metal in the electrolyte, as illustrated in Fig. 1, leads to fast but controllable lithium pre-doping of graphite anode without any safety issues, such as exothermic explosive behavior, rapid temperature rise, and electrolyte degradation [26]. Compared with conventional EC and ESC methods, because of the formation of almost zero-gap between graphite and lithium electrodes, the DC method provides not only extremely faster lithium diffusion rate but also much faster pre-lithiation rate. The AC/graphite full-cells pre-doped through DC method exhibited remarkably higher coulombic efficiency and longer cycle life, especially at short doping time.

However, there still remains considerable uncertainty in understanding the DC pre-lithiation method. In the case of conventional EC method, lithium doping and de-doping (charging and discharging of graphite electrode) can be monitored using electrochemical methods, such as tracing current and voltage profiles, as shown in Fig. S2. The electrochemical analysis gives us very useful analytical information not only on the degree of lithiation of graphite electrode but also on the phase of graphite electrode [27–29]. Dahn reported very well-organized experimental results on the phase behavior of lithium-intercalated graphite compounds through the combination of electrochemical method and in situ X-ray diffraction technique [30]. Because chemical potential values of Li in coexisting phases are equal according to the simple thermodynamics rule, the coexisting phase regions appear as plateaus in plots of the voltage V(x,T) of Li/LixC6 cells versus x at constant temperature of T in the electrochemical analysis. Dahn observed that graphite electrode experiences several phase transitions during lithiation in this order: graphite → stage 1′ → stage 4 → stage 3 → stage 2L → stage 2 → stage 1, as degree of lithiation increases. However, DC method does not need to form the electrochemical circuit during lithiation. That is a robust advantage in the viewpoint of simplicity and cost efficiency. Unfortunately, however, the simplicity advantage prevents understanding of DC method, because electrochemical analysis cannot be carried out during DC lithiation.

Here, we directly investigated the structural change behavior of graphite electrode during the DC pre-lithiation through in situ synchrotron wide-angle X-ray scattering (WAXS) measurements in transmission mode to uncover the uncertainty on the phase behavior of graphite anode during DC pre-lithiation. The DC method revealed much faster phase transformation behavior than the conventional EC and ESC methods, verifying that DC method provides faster lithiation rate of graphite electrode.

2. Experimental

2.1. Materials

Lithium metal (Honjo Metal, Japan), a graphite electrode consisting of 90 wt % graphite, and 10 wt % binder with a copper current collector were used. A battery-grade electrolyte solution of 1.0 M LiPF6 in ethylene carbonate/diethyl carbonate (3/7, v/v) mixture (Soulbrain, Republic of Korea) was used. A porous polyolefin membrane (Celgard 2320 Trilayer, USA) with a thickness of 20 μm was used as a separator. High quality aluminum laminated plastic film (D-EL40H, Linyi Gelon Lib, China) was used for the fabrication of pouch cell.

2.2. In situ synchrotron WAXS examination

In the in situ synchrotron WAXS examinations, all of the pre-lithiation experiments were performed with the graphite/Li

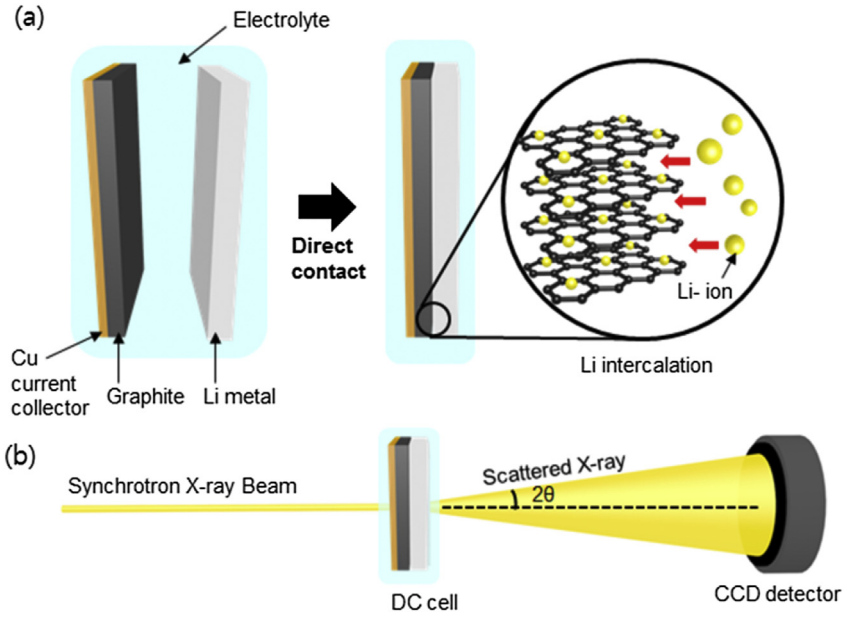

Fig. 1. Schematic illustration of (a) DC pre-lithiation process and (b) in situ synchrotron WAXS measurement setup.