

Direct Observation of the SEI Layer Formation Process on the Graphite Anode by *in situ* TEM

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Graphite is currently the primary anode material used in most lithium ion batteries (LIB), which is due to its high abundance, low price, high stability and long cycle life [1]. Given the low capacity of graphite (372 mAh g⁻¹), a commonly used approach is to mix the silicon (4200 mAh g⁻¹) with graphite to increase the overall capacity of the anode [2]. This is also done to match the increased capacity of the anode side, with high-capacity cathode materials, such as nickel-rich cathode materials, which have been developed to deliver high energy density [3][4]. Moreover, new electrolytes and impact of the additives also must be explored to fully understand the degradation processes at the electrolyte/electrode interfaces leading to formation of both solid electrolyte interface (SEI) on the anode side and cathode electrolyte interface (CEI) on the cathode side, affecting overall battery performance [5][6].

In this work, we report *ex situ* and real-time *in situ* (scanning) transmission electron microscopy ((S)TEM) characterization of the SEI layer formation on the graphite anode. The graphite anode was studied after charge and extended soak in the 1M LiPF₆ in ethylene carbonate and ethyl methyl carbonate (3:7, v:v), LP57, electrolyte. The *ex situ* high-resolution TEM (HRTEM) images show that the graphite (002) lattice plane remains after charge (Figure 1a) with two distinct SEI layer components such as Li₂O and Li₂CO₃, observed at ambient temperature of 22 °C on the basal plane of the graphite anode (Figures 1b and 1c). The elemental mapping of carbon and other possible elements of the SEI, such as oxygen, fluorine, and phosphorus, can be observed from the energy-dispersive X-ray spectroscopy (EDS) analysis (Figure 1d).

Further, to fully understand the intercalation mechanism of Li⁺ ions into the graphite anode and SEI layer formation, we performed *in situ* TEM experiments. The initial data indicate that after the first charge the graphite (002) plane remains, while a thin layer of approximately 2 nm forms on the surface of the graphite anode (Figure 2). This SEI layer is composed of Li₂O (111) and Li₂CO₃ (002), and preferentially forming along the basal plane of graphite, which is consistent with the *ex situ* TEM observation. Further studies will focus on the effect of electrolyte additive combinations on the SEI layer formation and stability [7].

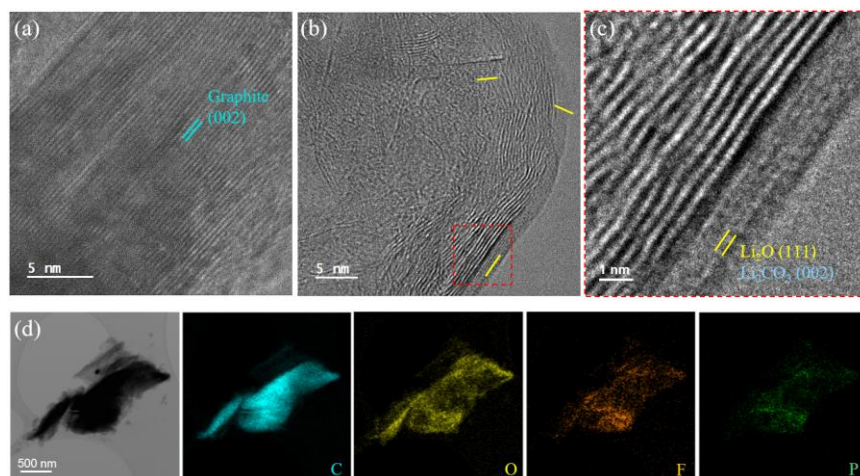


Figure 1. *Ex situ* TEM images showing the structure and morphology of graphite anode after charge and soaked in LP57 electrolyte: (a) graphite (002) lattice plane, (b) SEI formation on the surface, and (c) interface between graphite and SEI. The red dashed square in Figure 1b indicates the location of SEI-graphite interface in Figure 1c. (d) EDS mapping showing the elemental distribution of carbon, oxygen, fluorine, and phosphorus.

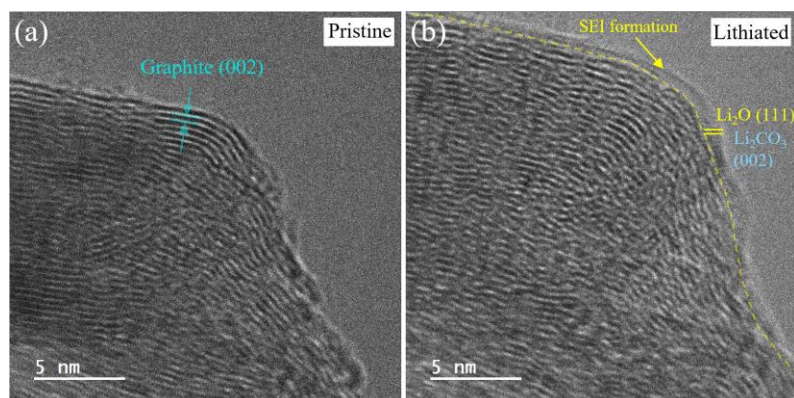


Figure 2. *Operando* HRTEM images showing (a) pristine graphite with (002) lattice plane before the charging process and (b) SEI formation in the form of Li_2O and Li_2CO_3 on the surface after *in situ* TEM charging process. The SEI-graphite interface is indicated by the yellow dashed line.

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