

Nanoscale Dynamics of Electrochemical Sodiation of CF_x Unveiled by in-situ TEM: A Comparative Study with Lithiation

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Graphite fluoride (CF_x) is the most potential and promising cathode material choice in lithium (Li) and/or sodium (Na) primary batteries, owing to the significantly high theoretical special capacity and theoretical energy density. Li/ CF_x batteries have been partially used, such as military portable power sources, but Na/ CF_x batteries are still being studied in the laboratory. The inherently poor electronic conductivity and dynamics performance of CF_x limits its extensive popularization. In this regard, it is necessary to study the microcosmic dynamic processes of electrochemical lithiation and sodiation of CF_x , and the differences between them.

Herein, the electrochemical lithiation and sodiation processes of CF_x nanosheets were investigated by in-situ transmission electron microscopy (TEM) platform. It turns out that the sodiation kinetics differs significantly from the lithiation kinetics of CF_x nanosheets. During the sodiation process of CF_x nanosheet, the reaction occurs immediately after a constant potential is applied to Na anode with respect to CF_x cathode. There exists an obvious sodiation reaction front, which advances more and more slowly as time goes on. By contrast, it takes a while for the lithiation reaction to occur after the constant voltage is applied. And once the lithiation reaction initiates, the lithiation of the whole CF_x nanosheet completes within a few seconds without an obvious reaction front. We propose that the difficulty of ionization of metallic Li and Na and the diffusion coefficient of Li^+ , Na^+ and e^- in the surface or interior of CF_x raise the different phenomenon. The comparison of the reaction kinetics between the sodiation process and the lithiation process of CF_x nanosheets reveals an important new insight for fundamental understanding of the nanoscale dynamics.

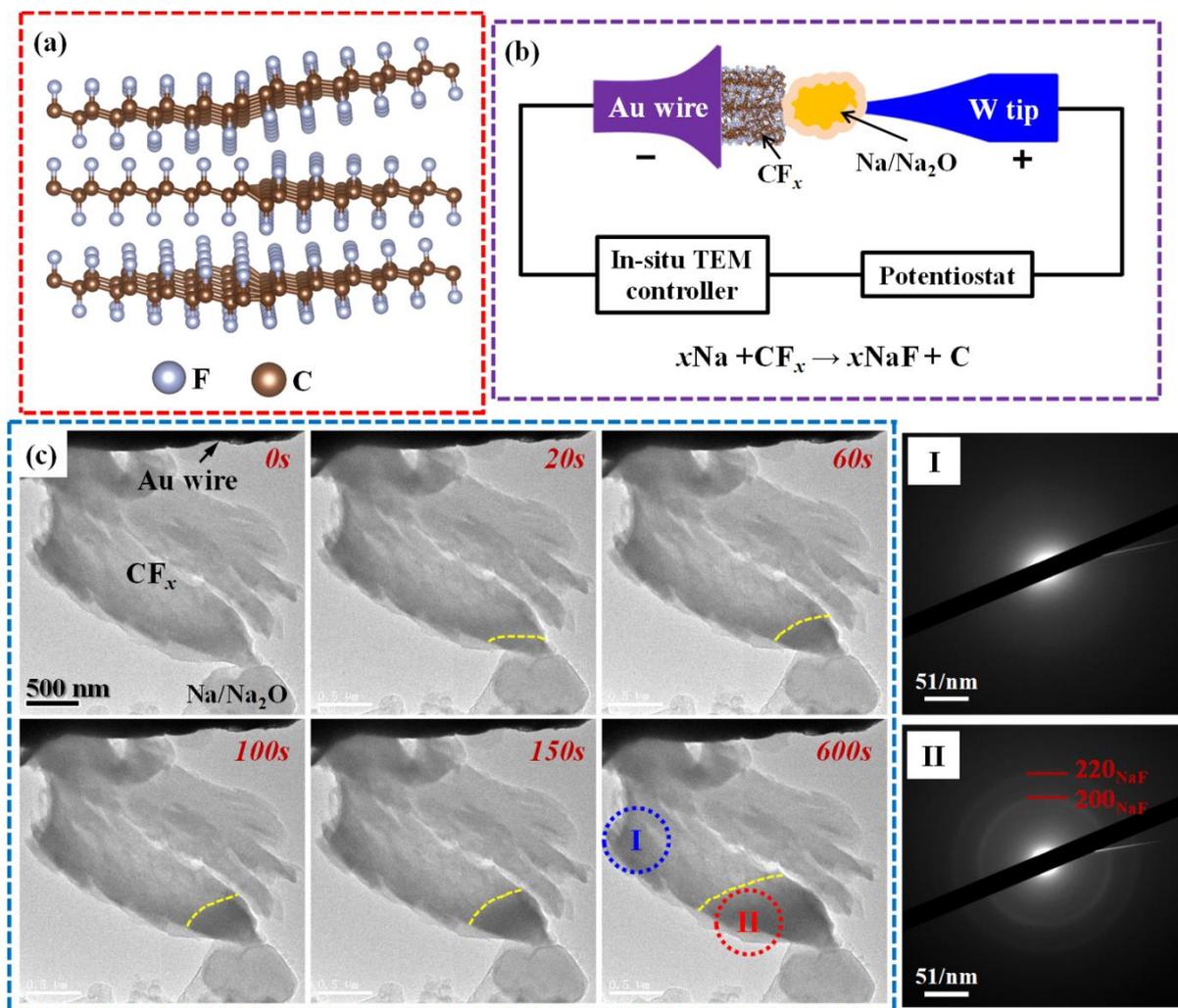


Figure 1. (a) The schematic diagram of amorphous structure of CF_x. The CF_x utilized in this research is amorphous. (b) (top) Schematic of in situ TEM experimental setup, where the metallic Na, Na₂O, and CF_x nanosheet serve as the counter electrode, electrolyte, and working electrode, respectively. (bottom) The overall sodiation reaction equation of CF_x. (c) A series of time-lapse TEM images of the different sodiated stage of CF_x nanosheet at six time points. An obvious sodiation reaction front advances gradually with time. The SAED patterns of area I and II (pristine and sodiated area) marked by the yellow and red dotted circle are shown on the right. Differing from the halo ring of SAED pattern of pristine area, there are two distinct sub-enclosing Bragg circles in the SAED pattern of sodiated area, which can be indexed as the cubic NaF phase.

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