

Reaction Mechanism and Kinetic of Graphene Supported Co_3O_4 Nanocubes with Lithium and Magnesium Studied by *in situ* TEM

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While most of current research on energy storage is focused on lithium-ion battery, the alternatives like magnesium and aluminum has many obvious advantages. For example, magnesium is a nature abundant element being the 5th most abundant element in the earth's crust. It is environmentally friendly, low price and has many safe characters, *i.e.* it is stable enough in ambient atmosphere to handle. However, currently there are many serious limitations in magnesium electrochemistry that prevents magnesium-ion battery being an efficient system for energy storage. In this work, by using high resolution *in-situ* transmission electron microscopy (TEM) the diffusion of multivalent ions and the solid-state reactions with Co_3O_4 nanocubes and graphene have been studied, in order to explore the reaction mechanism for multivalent-ion batteries, in direct comparison to that of lithium-ion battery. Nano-composite materials, especially graphene-based nanostructure¹⁻² have been developed for high-capacity anode materials showing enhanced high electron and lithium ion conductivity by graphene. Meanwhile, the emerging *in-situ* transmission electron microscopy (TEM) techniques with localized electrical measurement capabilities provide a practical platform to investigate electrochemical reactions in Li-ion battery materials by building a full or half "nano-cell" inside the TEM specimen chamber¹⁷. Such real-time observations of dynamic composition and microstructural evolution in the electrochemical reaction have provided many novel clues to understand the lithiation/de-lithiation mechanisms at nano or even atomic-scale for several novel anode materials¹⁸. Herein, we report a morphological and structural study of graphene sheets supported Co_3O_4 nanocubes during the electrochemical reaction with lithium, and magnesium.

Upon charging with lithium-ions, the Co_3O_4 nanocubes decompose to small Co metal nanoparticles (2-3 nm) and embedded in as-formed Li_2O matrix; reversely, the CoO nanoparticles formed on the site of Co accompanying the decomposition of Li_2O in the discharging process. The lithiation process is dominated by surface diffusion of Li^+ and graphene sheets enhance the Li^+ diffusion leading to a fast charging process. However, upon charge with magnesium, the Mg^{2+} diffusion is sluggish and there is no sign of conversion reaction between Mg and Co_3O_4 at room temperature. Instead, a thin film consisting of metal Mg nanoparticles is formed on the surface of graphene due to a process similar to metal plating. The Al^{3+} diffusion is even more sluggish and there is no electrochemical reaction between Al and Co_3O_4 can be observed at room temperature. The finding may shed light on the development of batteries with high energy density based on multivalent ions other than lithium.

References:

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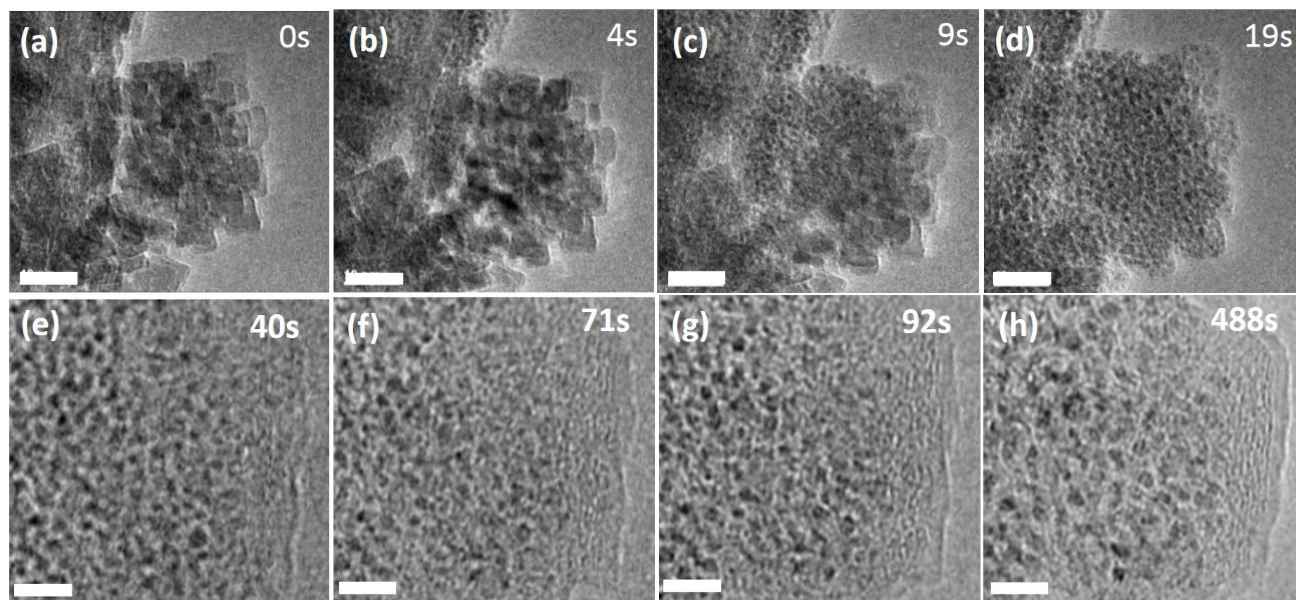


Figure 1. Time-resolved TEM images of electrochemical lithiation process (a) to (d); and delithiation process (e) to (h) of Co_3O_4 nanocubes on graphene. The scale bar is 10nm.

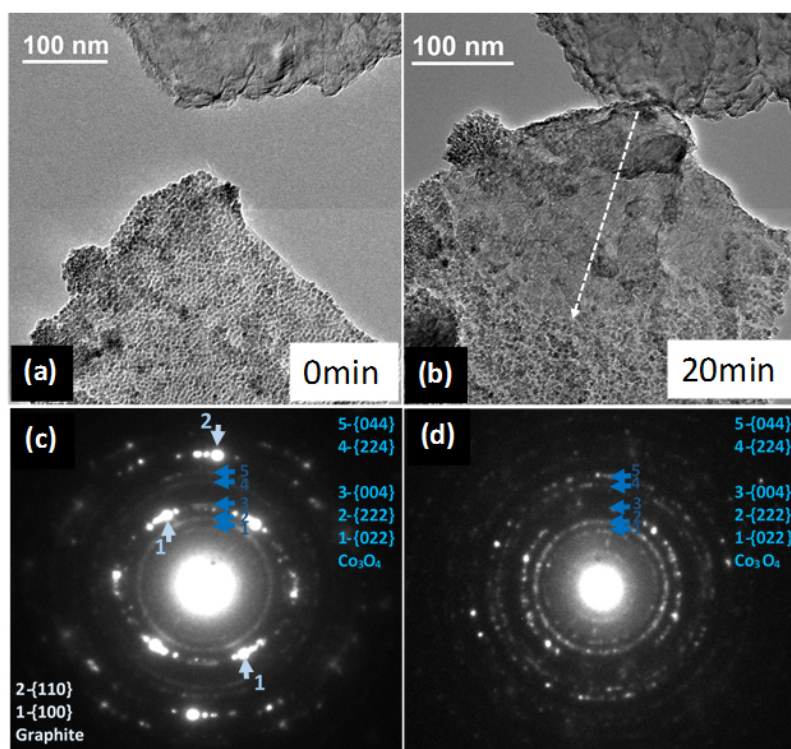


Figure 2. Microstructural evolutions in the magnesiation process. (a) The MgO/Mg probe and the Co_3O_4 /Graphene nanocomposites loaded on a Au tip, prior to the electrochemical magnesiation. (b) TEM image of the reaction front of magnesiation after the electric bias of -5 V has been applied. The front moves forward about 240 nm in 20 minutes. (c) SAED pattern of Co_3O_4 /Graphene nanocomposites before the magnesiation reaction. (d) SAED pattern of Co_3O_4 /Graphene nanocomposites after the magnesiation reaction.