

Tackling Reversible Conversion Reaction Mechanism for Lithium Based Battery

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The demand for next generation of lithium based batteries with higher capacity and rate as well as increased cycle and calendar life requires new lithium storage and transfer mechanisms beyond what current lithium ion battery technique could provide. In lithium based battery, the lithium ions are stored in electrode materials either by physically intercalating (e.g. LiCoC_2) or chemically alloying (e.g. Li_xSi). In the past decade, the conversion reaction of 3d metal oxide nanostructures which involves the formation and decomposition of lithium compounds in nanoscale present an array of advantages [1]. Despite a large number of synthesis and performance studies, the underlying mechanisms involving structural and phase changes during the lithiation/delithiation processes of these nanostructures has little been tackled.

The emerging in-situ transmission electron microscopy (TEM) techniques with localized electrical measurement capabilities provide a practical platform for investigating electrochemical reactions in Li-ion battery materials by building a full or half “nano-cell” inside the TEM specimen chamber [2]. 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 atomic-scale for several novel anode materials. Herein, we report a comprehensive morphological and structural study to tackle the conversion reaction mechanisms during the lithiation/delithiation process by using graphene sheets supported Co_3O_4 nanocubes as a model system.

The graphene supported Co_3O_4 nanocubes were synthesized by simple hydrothermal method. As shown in HAADF STEM image fig. 1A and HRTEM image in fig. 1C, these nanocubes with a size of $\sim 5\text{nm}$ are dispersed on graphene sheets with Co_3O_4 phase confirmed by diffraction pattern in fig. 1B. The in-situ TEM experiments were performed on a specified electrical probing TEM holder with a dual-probe design as shown in Fig. 1D, i.e. one Au rod is used as the sample holder with a small amount of Co_3O_4 /Graphene dispersed on its tip; on the other side a STM tungsten (W) probe driven by Piezo-motor capable of 3-D positioning is used to mount Li metal. The W probe tip was scratched by Li metal strip and then affixed on the TEM holder inside a glove box, then transferred to TEM column with limited exposure to air ($<5\text{ s}$), when a layer of lithium oxide was grown on the surface of Li metal acting as a solid electrolyte for the nano-cell Li-ion batteries.

Time-resolved snapshots shown in fig. 2(a) to (d) and (e) to (h) present the electrochemical lithiation and delithiation process of a cluster of Co_3O_4 nanocubes on graphene sheets, respectively. As the lithiation occurs, pristine structure of Co_3O_4 nanocubes with a size of 5nm decompose to $1\text{-}2\text{nm}$ nanoparticles embedded in a matrix. The real time observation reveals the reaction starts from the contacting point between $\text{Li}_2\text{O}/\text{Li}$ and Co_3O_4 -Graphene and the interface between unreacted and reacted areas is clearly seen throughout the process which indicates the lithiation process is a rate-limiting

process which is determined by either the Li^+ diffusion through the surface of graphene or the reaction rate of Li^+ and Co_3O_4 . In the reverse process, the as-formed Co nanoparticles embedded in Li_2O matrix in fig. 2(e) didn't change in the first 60s of incubation time. Then, the Co nanoparticles start to decompose into smaller nanoparticles and new nuclei form on the site of the Co nanoparticles at the same time until a saturation density of nuclei is reached as seen in fig. 2(f). Within 5 mins, the newly formed phase grew into 1-3nm nanoparticles while the Li_2O matrix is gradually consumed which is evidenced by that the flake-like Li_2O shown in fig. 2(e) changed to clear graphene sheets in fig. 2(h) after the reaction. These observation reveals that both lithiation/delithiation processes are accompanied by the formation of new phase ($\text{Li}_2\text{O}/\text{Co}$ oxides) on the site of decomposed $\text{Co}_3\text{O}_4/\text{Co}$ nanoparticles in the matrix. The structure of Co nanoparticles densely embedded in Li_2O matrix on graphene sheets is critical for the reverse reaction to happen because the large chemical barrier for the decomposition of Li_2O is lowered by small metal nanoparticles with large surface area and catalytic properties. The graphene sheets play as a supporting materials and ion/electron transport promoter without changing their own structures.

Reference:

- [1] Arico, A. S., Bruce, P., Scrosati, B., Tarascon, J.-M. & van Schalkwijk, W. *Nat Mater* **4** (2005), 366.
 [2] Huang, J. Y. Zhong, L., Wang, C. M. et al. *Science* **330** (2010), 1515.

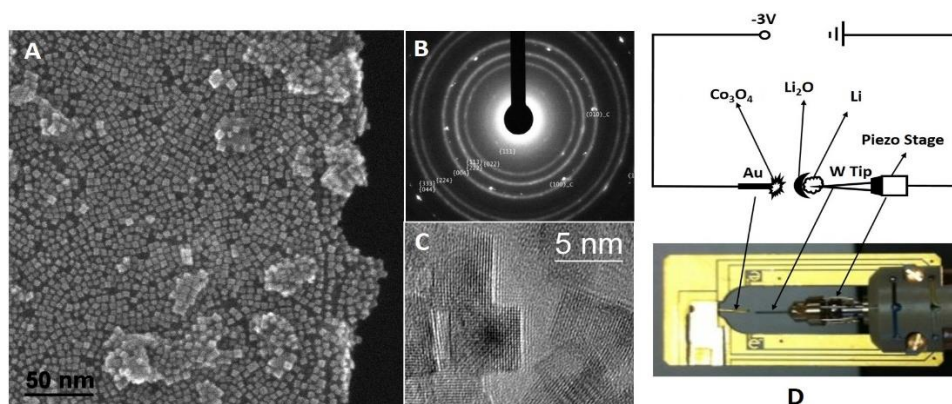


Fig. 1 As synthesized Co_3O_4 nanocubes on graphene: A. STEM Z-contrast, B. Electron diffraction, and C. HRTEM images; schematic and real layout of the TEM holder.

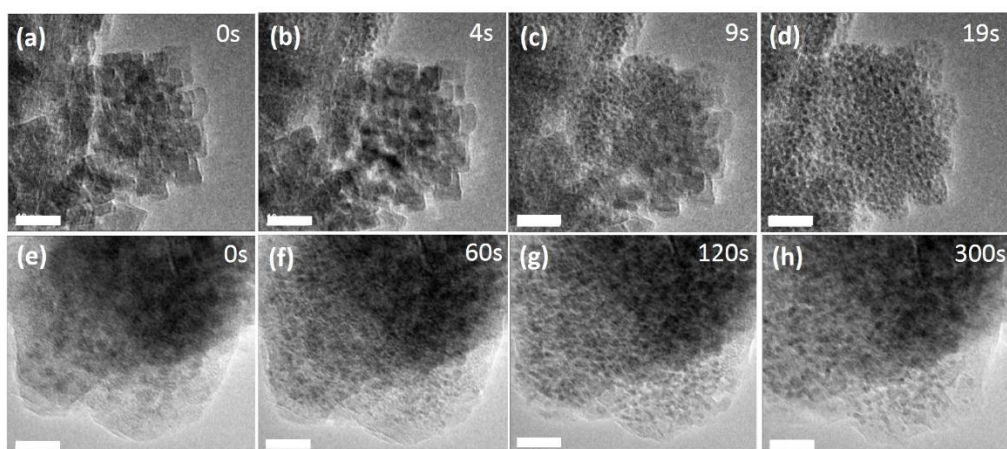


Fig.2 Time-resolved TEM images of lithiation (a-d) and delithiation (e-h) processes of $\text{Co}_3\text{O}_4/\text{graphene}$.