

## Real Time Observation of Initial Conversion Reaction of $\text{Co}_3\text{O}_4$ Nanoparticles Using Graphene Liquid Cell Electron Microscopy

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Transition metal oxides (TMOs) have been noticed as candidates of anode materials for lithium ion batteries (LIBs) due to their high theoretical capacity.  $\text{Co}_3\text{O}_4$  have been studied in many research groups, as an example of TMOs [1,2]. Initial Conversion reaction dynamics of TMOs including  $\text{Co}_3\text{O}_4$  is important as the products are irreversible and give much effect to subsequent cycling reactions. For better design of advanced LIB, it is necessary to understand detailed mechanism of reaction process conversion reaction.

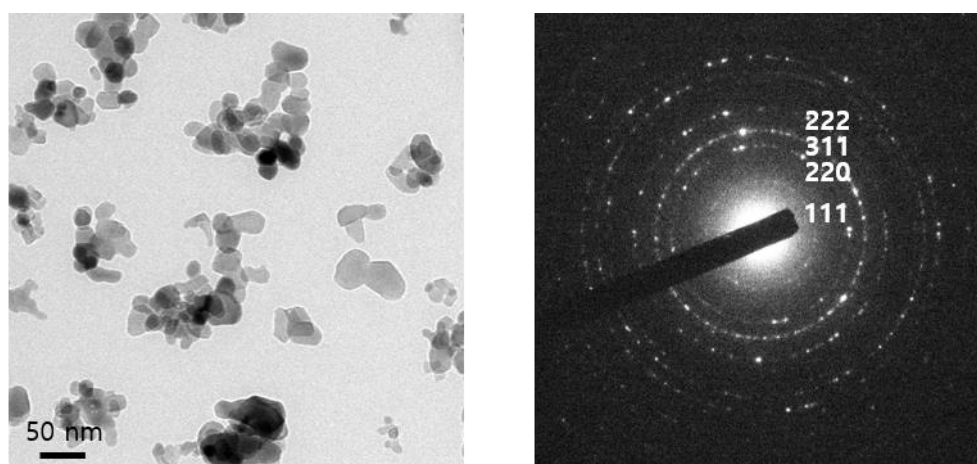
To reveal the mechanisms of such reactions, *in situ* transmission electron microscopy (*in situ* TEM) is a suitable technique because it can provide structural and chemical information of nanosized materials. Among many methods of *in situ* TEM, graphene liquid cell transmission electron microscopy (GLC-TEM) is a realistic way to observe lithiation behavior inside liquid electrolyte, along with advantage of high resolution TEM (HRTEM) analysis [3,4].

For experiment,  $\text{Co}_3\text{O}_4$  nanoparticles were dispersed in liquid electrolyte (1.3 M of  $\text{LiPF}_6$  in ethylene carbonate (EC): diethyl carbonate (DEC) in 3:7 (v/v) with 10 wt% of fluoroethylene carbonate (FEC)). Figure 1(a) shows TEM image of pristine  $\text{Co}_3\text{O}_4$  nanoparticles. The average size of the particles were 20 – 50 nm. Figure 1(b) is the corresponding diffraction pattern, showing spinel structure of  $\text{Co}_3\text{O}_4$ . For real time observation, GLC was fabricated by encapsulating liquid mixture between two graphene sheets, as same method with previously reported literature [4]. When electrons are supplied from electron beam from TEM gun, Li ions are reduced and lithiation of  $\text{Co}_3\text{O}_4$  nanoparticles started. Figure 2 shows time-series TEM images of lithiation of  $\text{Co}_3\text{O}_4$  nanoparticles. At 0 s,  $\text{Co}_3\text{O}_4$  particles were unreacted and immersed in liquid electrolyte. At 55 s, the particle locating at left part (marked as red arrow) was transformed into amorphous matrix and particles (size of 1 – 3 nm) embedded in it. Also, another particle started to react (marked as green arrow). Subsequently at 90 s, the particle was lithiated, similar to the previous one (marked as yellow arrow). Finally at 260 s, all  $\text{Co}_3\text{O}_4$  particles were reacted with Li. The product of this lithiation is likely to amorphous  $\text{Li}_2\text{O}$  and metallic Co particles, as reported previously [5,6].

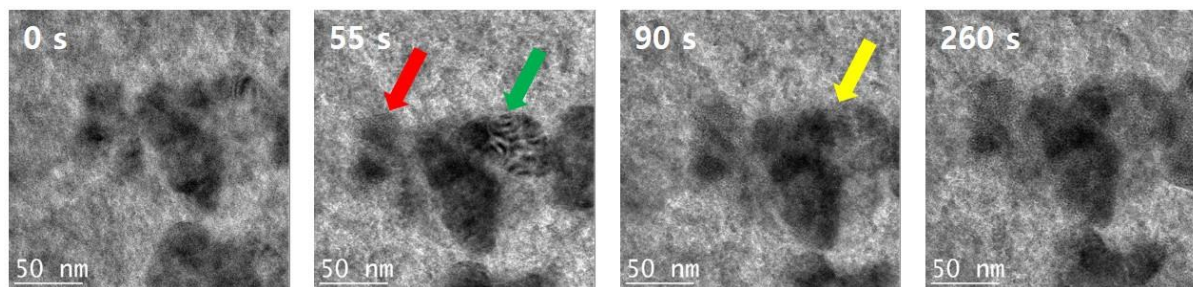
In summary, morphological dynamics of  $\text{Co}_3\text{O}_4$  nanoparticles were observed using GLC-TEM. Upon lithiation, morphology of the particles were observed as pristine nanoparticles turned into amorphous matrix and tiny particles embedded in it. We believe understanding such initial behavior of lithiation will contribute to better design of advanced LIBs using nanostructured  $\text{Co}_3\text{O}_4$  anode [7].

## References:

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[7] The authors acknowledge the funding from Korea CCS R&D Center (KCRC) grant by the Korea government (Ministry of Science, ICT & Future Planning) (No. NRF-2014M1A8A1049303), Wearable Platform Materials Technology Center (WMC) (NR-2016R1A5A1009926), and Institute for Basic Science (IBS) (IBS-R004-G3).



**Figure 1.** (a) TEM image of  $\text{Co}_3\text{O}_4$  nanoparticles and (b) diffraction pattern.



**Figure 2.** Time-series TEM images of lithiation of  $\text{Co}_3\text{O}_4$  nanoparticles.