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Real Time Observation of Initial Conversion Reaction of Co_3O_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. Co_3O_4 have been studied in many research groups, as an example of TMOs [1,2]. Initial Conversion reaction dynamics of TMOs including Co_3O_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, Co_3O_4 nanoparticles were dispersed in liquid electrolyte (1.3 M of $LiPF_6$ 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 Co_3O_4 nanoparticles. The average size of the particles were 20 – 50 nm. Figure 1(b) is the corresponding diffraction pattern, showing spinel structure of Co_3O_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 Co_3O_4 nanoparticles started. Figure 2 shows time-series TEM images of lithiation of Co_3O_4 nanoparticles. At 0 s, Co_3O_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 Co_3O_4 particles were reacted with Li. The product of this lithiation is likely to amorphous Li_2O and metallic Co particles, as reported previously [5,6].

In summary, morphological dynamics of Co_3O_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 Co_3O_4 anode [7].

References:

[1] Xue, X. *et al*, Chem. Commun **47** (2011), p. 4718.
[2] Chen, Y. M. *et al*, Angew. Chem. Int. Ed. **55** (2016), p. 5990.
[3] Yuk, J. M. *et al*, ACS Nano **8** (2014), p. 7478.
[4] Cheong, J. Y. *et al*, Nano Energy **25** (2016), p. 154.
[5] Li, J. *et al*, ACS Nano **16** (2016), p. 9577.
[6] Su, Q. *et al*, Nano Energy **9** (2014), p. 264.
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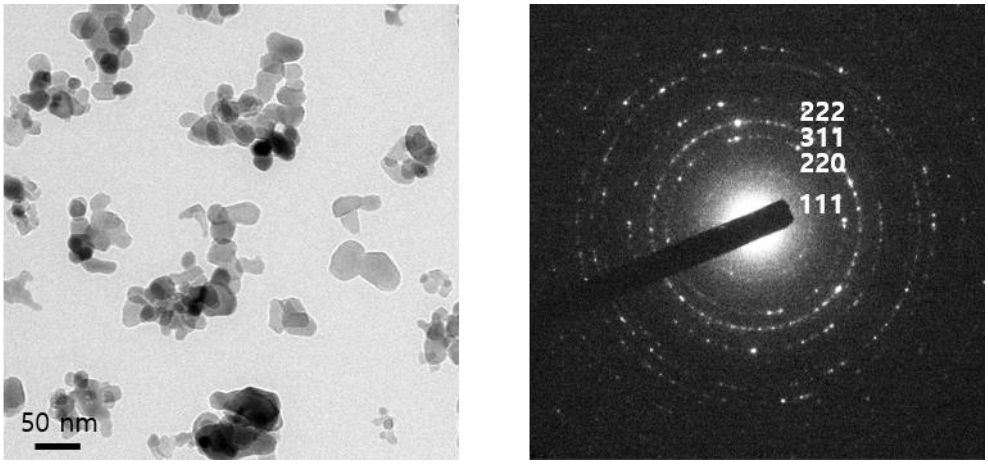

Figure 1. (a) TEM image of Co_3O_4 nanoparticles and (b) diffraction pattern.

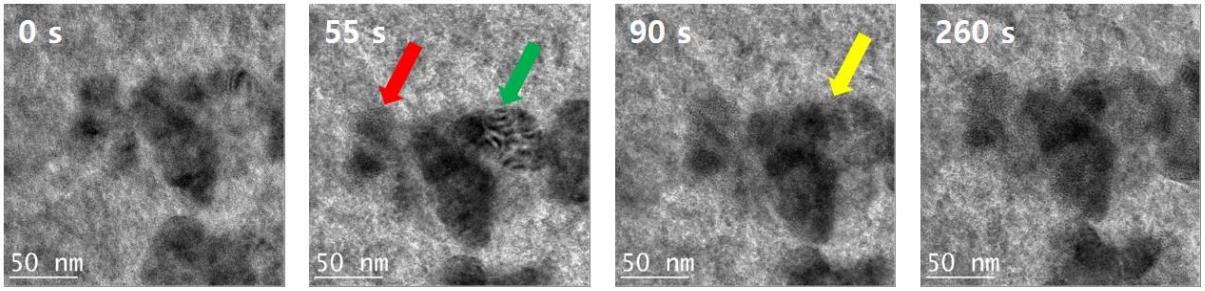

Figure 2. Time-series TEM images of lithiation of Co_3O_4 nanoparticles.