

***In Situ* TEM Study on the Growth Process of Amorphous Layer on SnO₂ Nanoparticle During Sodiation on Real Time Scale**

Jun Young Cheong¹, Joon Ha Chang^{1,2}, Jeong Yong Lee^{1,2} and Il-Doo Kim¹

¹. Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea

². Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon, Korea

As the secondary rechargeable batteries, lithium-ion batteries (LIBs) have been commercialized, to some extent, in different applications, such as electric vehicle (EV), cell phones, cameras, and other small-scale electronic devices [1,2]. Nevertheless, relatively scarce amount of lithium (Li) present in the world can significantly downplay its commercialization in the far future, because there is increasing demand for large-scale electric grid or energy storage system that can be devised in a cost-effective way. In order to overcome the limited Li resources, different alternative batteries have been suggested. [2] Among them, sodium-ion battery (SIB) has become one of main feasible and practical candidates mainly due to the abundance and cheap cost that sodium (Na) can offer, compared with Li.

Since the initial discovery of SIBs, many different materials have been researched for their potential applications as electrodes for SIBs [3]. Among them, Sn-based materials (Sn, SnO₂, and others) have attracted much attention due to their high theoretical capacity, abundance, and suitable electrochemical reactions with Na [4,5]. However, although significant studies on utilizing different nanostructures for Sn-based materials have taken place, little is still known about the sodiation behaviour of Sn-based materials. Especially, understanding on how their interfacial properties change in the process of sodiation is significantly limited, though it is an important part to investigate. Therefore, here we have investigated how the interface of SnO₂ nanoparticles actually changes in the process of sodiation in real time scale through transmission electron microscopy (TEM) using graphene liquid cell (GLC). Monolayer graphene was fabricated by chemical vapor deposition (CVD) process. Subsequently, SnO₂-containing electrolytes are encapsulated between the two graphene sheets, which were loaded on TEM grid. Upon e-beam irradiation, the electrolytes in GLC are decomposed and move towards the active material [6], which allow us to observe the sodiation process in real time. SnO₂ nanoparticle was immersed in the propylene carbonate (PC)-based electrolytes, where sodiation process takes place in all directions of the nanoparticle.

High resolution transmission electron microscopy (HRTEM) image of SnO₂ nanoparticle is shown in Figure 1. It clearly shows that the crystal structure of SnO₂ nanoparticle is cassiterite structure. Figure 2 shows the morphological evolution of the interface of SnO₂ nanoparticles, from 0 s to 412 s. In the initial state (0 s), SnO₂ nanoparticles are surrounded by the electrolyte, where it does not have any interfacial films. In the process of sodiation, large decomposed electrolytes start depositing on the nanoparticle (190 s) and subsequently forms outer interfacial layers on some parts of the nanoparticle (340 s). Finally, at 412 s, it is clearly shown that the amorphous layer is formed on the outer surface of SnO₂ nanoparticle, where it has relatively uniform thickness. In addition, at 412 s, particle-layer boundary is firmly established.

In summary, we have shown, through GLC, that the amorphous layer is formed on the SnO₂ nanoparticle immersed in the electrolyte during sodiation. Investigation of interfacial dynamics of

electrode materials can be possible utilizing in-situ TEM observation using GLC. [7]

References:

- [1] P. G. Bruce, B. Scrosati and J.-M. Tarascon, *Angew. Chem. Int. Ed.* **47** (2008), p. 2930-2946.
- [2] P. G. Bruce *et al*, *Nat. Mater.* **11** (2012), p. 19-29.
- [3] S.-W. Kim *et al*, *Adv. Energy Mater.* **2** (2012), p. 710-721.
- [4] D. Su, H.-J. Ahn and G. Wang, *Chem. Commun.* **49** (2013), p. 3131.
- [5] Y. Wang *et al*, *Electrochem. Commun.* **29** (2013), p. 8-11.
- [6] J. M. Yuk *et al*, *ACS Nano* **8** (2014), p. 7478-7485.
- [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), End-Run grant from KAIST by the Korea government in 2015 (Ministry of Science, ICT & Future Planning) (N01150615), and Institute for Basic Science (IBS) (IBS-R004-G3).

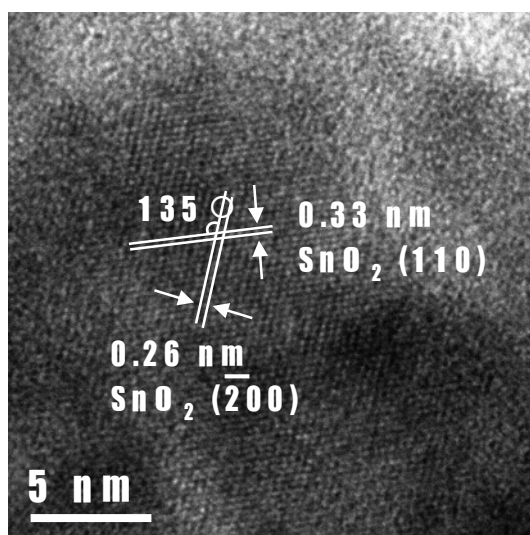


Figure 1. HRTEM image of SnO₂ nanoparticles showing lattice fringes of crystal structure.

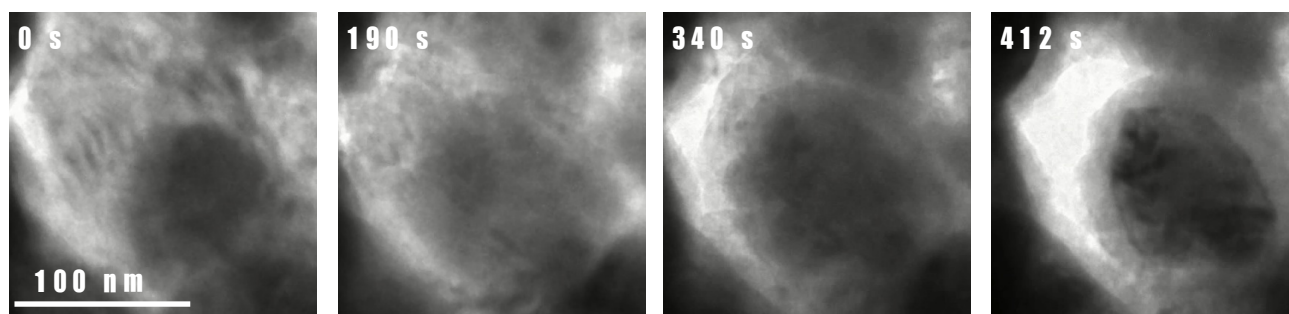


Figure 2. Time-series TEM observation images showing the growth process of amorphous layer on SnO₂ nanoparticles.