**In Situ** TEM Observation on the Growth of Solid Electrolyte Interphase (SEI) Layer on Co$_3$O$_4$ upon Sodiation and Magnesiation using Graphene Liquid Cell

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The real time observation of interfacial properties of nanoparticles in high resolution has attracted considerable attention, as it can provide the fundamental understanding that is crucial to fabricate rationally designed materials with more suitable interfaces. In this aspect, graphene liquid cell has been sought after by a number of researchers, due to its easy fabrication and high resolution imaging readily available [1].

In the recent times, the application of graphene liquid cell has been extended to the battery fields, where various dynamics such as the anisotropic volume changes and conversion dynamics were also observed [2,3]. To observe the dynamics of interfaces of electrode materials, it was previously shown that the graphene liquid cell can be employed to observe the growth dynamics of solid electrolyte interphase on anode materials, such as SnO$_2$ in the previous study [4,5]. Upon the decomposition of electrolytes (1.3 M of lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate (EC):diethylene carbonate (DEC) (v/v = 3:7) with 10 wt% of fluoroethylene carbonate (FEC)), the electrolytes are reduced and LiPF$_6$ is reduced to Li atom, where Li triggers the overall lithiation. The process is generally e-beam induced lithiation, where the decomposition of electrolytes and the build-up of solid electrolyte interphase layer were visualized. Nevertheless, up to this point, not much study has yet been delved into directly observing the interfacial properties of electrode materials upon sodiation and magnesiation, which are some of the highly sought-after next-generation rechargeable battery systems [6,7]. The question still remains, among many researchers, whether the graphene liquid cell can also be tuned in such a manner to observe the interfacial dynamics of various electrode materials upon sodiation and magnesiation.

In this work, we have conducted *in situ* TEM observation on the growth dynamics of solid electrolyte interphase (SEI) layer on Co$_3$O$_4$ upon sodiation and sodiation, with the suitable electrolytes for each reaction inside the graphene liquid cell. TEM images of Co$_3$O$_4$ nanoparticles in the liquid electrolyte inside the graphene liquid cell are shown for both magnesiation and sodiation (Figure 1). For the electrolytes, 1 M of sodium perchlorate (NaClO$_4$) in propylene carbonate (PC) was used for sodiation, while 0.1 M of magnesium bis(trifluoromethanesulfonimide) (MgTFSI) in diglyme was used for magnesiation. Figure 2 shows the time-series TEM images showing the growth of interfacial layers along with the decomposition of electrolytes, in the case of sodiation and magnesiation. In both of the cases, it can be clearly seen that the SEI layer is grown on the surface of the Co$_3$O$_4$ nanoparticles, as can be seen by the formation of amorphous layer in the boundary of the nanoparticles, in accordance with the previous literature [4,5].

In summary, we have realized the direct observation of interfacial layers on electrode materials upon sodiation and magnesiation, which are important to probe into the mechanism for next-generation batteries. It can be demonstrated based on these results that the graphene liquid cell can be employed to observe the dynamics in alternative batteries in addition to lithium-ion batteries [8].
References:

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Figure 1. TEM images of Co$_3$O$_4$ nanoparticles in liquid electrolyte inside the graphene liquid cell used for (a) magnesiation and (b) sodiation. (scale bar = 100 nm for (a) and 200 nm for (b))

Figure 2. Time-series TEM images showing the growth of SEI layer on Co$_3$O$_4$ nanoparticles upon (a) magnesiation and (b) sodiation. (scale bar = 100 nm)