Investigation of the Effect of Graphene-encapsulation on the O₂ Release Phenomenon from Li_xCoO_2, Studied by *In-situ* Heating STEM/EELS

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A major challenge regarding the incorporation of Li-ion batteries into the large-scale applications is the safety concerns, that arise from non-equilibrium service conditions such as temperature rise, high cut-off voltage charging or mechanical damage. Under these circumstances, the oxide cathode decomposes and releases oxygen which then reacts exothermically with the decomposed organic electrolyte and can ignite the combustible components of the Li-ion battery [1]. Considering the significance of this issue, O_2 evolution from oxide cathodes has been studied with various experimental and computational techniques. Overall, it is understood that the extraction of Li ions from the cathode unit cell results in the formation of under-coordinated oxygen atoms, which destabilizes the structure. At elevated temperatures, these oxygen atoms break the bonds with the transition metals and form O_2 molecules leaving the structure. As a result, the layered structure will transform to spinel and rock salt phases, which contain less oxygen in their unit cell. Utilizing *in-situ* heating STEM/EELS analysis together with *ab-initio* molecular dynamic (AIMD) we have shown that the extent of oxygen-release and the phase transitions are dependent on the surface fraction and facet termination of the individual particles [2].

Considering the very low oxygen transfer rate (OTR) of graphene and its derivatives [3], high mechanical flexibility and chemical stability in electrochemical environments, we performed graphene-encapsulation on $LiCoO_2$ cathode particles to suppress the O_2 release reaction form $LiCoO_2$. To do so, we charged the surface of the $LiCoO_2$ particles to facilitate the self-assembly of cathode particles (with positive surface charge) with Graphene oxide nano-sheets (with negative surface charge). Achieving a 2nm conformal coating of reduced graphene oxide (rGO), consisting of 4-5 layers of 0.4 nm think rGO, on individual cathode particles was confirmed with SEM, Raman, XPS and TEM results (Figure 1A).

Studying the effect of graphene-encapsulation on the O_2 release phenomena was carried out by utilizing *in-situ* heating STEM/EELS analysis. In these experiments, samples were heated to 300 °C incrementally in 50 °C steps, utilizing Gatan heating holder. Based on our previous report [2], $Li_{0.5}CoO_2$ is thermally unstable and starts to release oxygen when heated to above 100 °C. This reaction, which results in the reduction of cobalt cations, can be quantified by analyzing the Co L edges in the EELS signal. Specifically, by measuring the cobalt L3, L2 edges ΔE value as a function of temperature and acquisition position, we can quantify the cobalt valence state at each point in our samples and effectively compare the bare and the graphene-encapsulated Li_xCoO_2. Figure 1B, illustrates the EELS results obtained from the outmost ~5 nm of the surface of particles. By analyzing the results based on cobalt L3, L2 edges ΔE value, it can be understood that Co valence change at the surface of the particle is effectively delayed by the presence of graphene layer. The reduction of Co from 3+ to 2.6+ that occurs at ~ 100 °C in bare $Li_{0.5}CoO_2$, is postponed to higher than 200 °C for the graphene-encapsulated sample. Also, further reduction of Co species to 2+ which is observed between 200-300 °C does not occur in the graphene-encapsulated sample up to 300 °C. It should be noted that lower signal to noise ratio in the

spectra from the graphene-encapsulated samples is due to shorter acquisition times to avoid electron beam damage to the graphene layer. Furthermore, we performed EELS line scanning at each temperature to track the extent of oxygen-release from the cathode particles. To compare the degradation extent in both samples, we considered the valence of 2.6+ as the degradation threshold and measured the degradation extent accordingly as a function of length in the bare and graphene-encapsulated samples at each temperature. Accordingly, by reaching to 100 °C, reduction of cobalt and oxygen-release occurs in a layer of 10 nm at the surface of the bare $Li_{0.5}CoO_2$ particles. However, graphene-encapsulated sample shows a higher thermal stability and reduction of cobalt can be seen in areas < 5nm from the surface of the sample after increasing the temperature to higher than 150 °C. When the temperature reaches 300 °C, the thickness of this damaged layer reaches 50 nm in the bare $Li_{0.5}CoO_2$, while it is only about 10 nm for the graphene-encapsulated sample. These observations have been explained by AIMD modeling in two ways; 1) graphene-coating does not allow the formation and release of O_2 molecules since oxygen species bond with carbon atoms from the rGO layer. 2) If O_2 is formed, graphene layer inhibits the release of oxygen, which results in a O_2 rich atmosphere underneath the rGO layer that hinders the further O_2 release from the surface of cathodes. This hypothesis is supported with the recent work from Karki *et al.* [4], where inhibiting the O_2 release from the cathode particles was achieved in O_2 atmosphere. Their environmental controlled *in-situ* heating STEM/EELS results suggest that, in O_2 atmosphere, oxygen-release and reduction of transition metals in the layered oxide cathode framework is significantly delayed and thus the structure is more stabilized under O_2 atmosphere condition.

Furthermore, TEM imaging, thermal analysis experiments, electrochemical cycling and impedance spectroscopy together with AIMD simulations have been performed in this study to fully characterize the effectiveness of the graphene-encapsulation on the abusive tolerance of Li_xCoO_2.

References:
[1] Ribière, P.; Grugeon, S.; Morcrette, M., Energy Environ. Sci. **5** (2012), p. 5271.
[2] Sharifi-Asl, S.; Soto, F. A.; Nie, A., Nano Lett. **17** (2017), p. 2165.
[3] Nair, R. R.; H. A. Wu; Jayaram, P. A., Science **335** (2012), p. 442.
[4] Karki, K.; Huang, Y.; Hwang, S., ACS Appl. Mater. Interfaces **8** (2016), p. 27762.
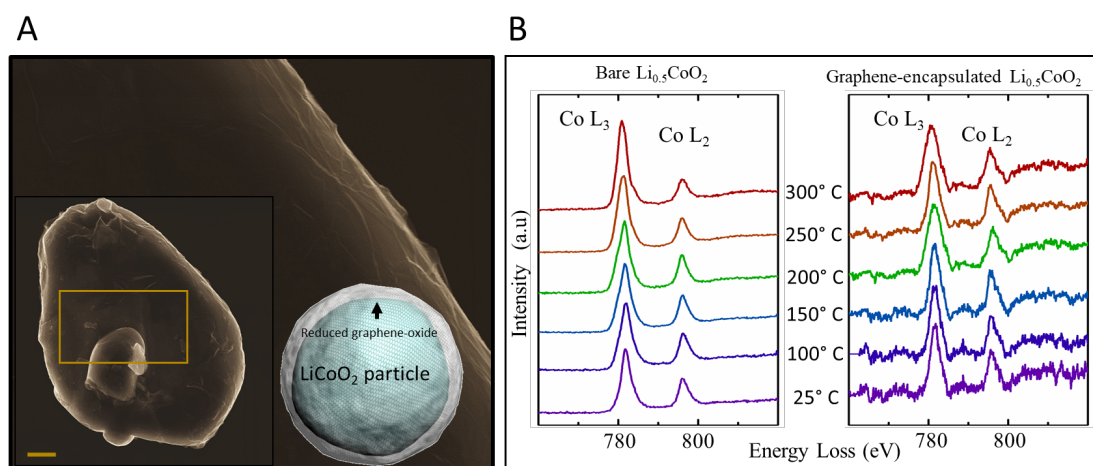
Figure 1. (A) SEM image from an individual graphene-encapsulated $LiCoO_2$ particle, with low magnification image and schematic depiction inset. (Scale bar is 1 μm in the inset image). (B) EELS spectra from the bare and graphene-encapsulated Li_xCoO_2 particles obtained during an *in-situ* heating experiment.