

## Investigating Side Reactions and Coating Effects on High Voltage Layered Cathodes for Lithium Ion Batteries

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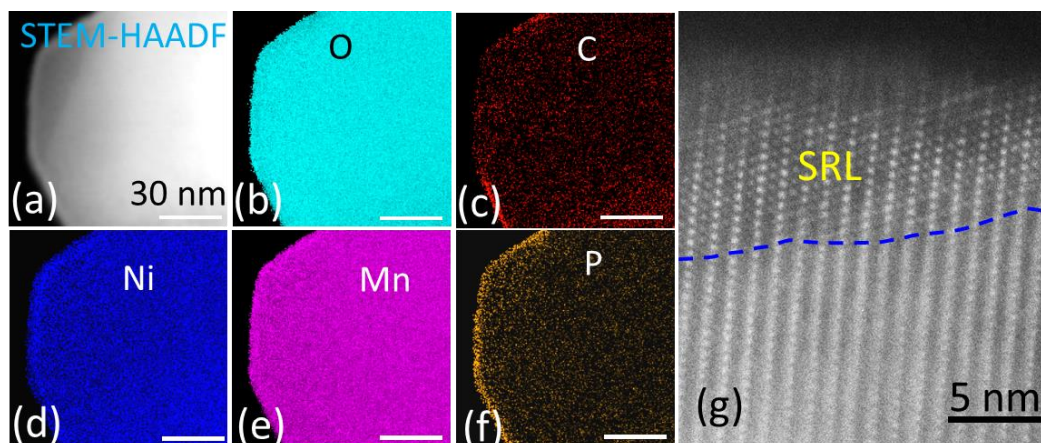
Immersion of a solid into liquid often leads to the modification of both the structure and chemistry of surface of the solid, which subsequently affects the chemical and physical properties of the system. For the case of the rechargeable lithium ion battery, such a surface modification is termed as solid electrolyte interphase (SEI) layer, which has been perceived to play critical role for the stable operation of the batteries. Especially for cathode that operated at high voltage windows, cathode/electrolyte side reactions will not only degrade electrolyte but also the cathode materials, which results in battery capacity and voltage fading.[1-3] However, the side reactions induced SEI layer on high voltage cathodes has not been fully understood. Its structure and chemical composition and its spatial distribution and dependence on the battery operating condition remain unclear.[4] Surface coating of cathode has been identified as an effective approach for enhancing the capacity retention of layered structure cathode.[5] However, the underlying operating mechanism of such thin coating layer, in terms of surface chemical functionality and capacity retention, remains unclear.

In this work, by using aberration corrected scanning transmission electron microscopy coupled with ultra-high sensitive energy dispersive x-ray spectroscopy, we probed the structure and chemistry of SEI layer on several high voltage cathodes. We show that layer-structured cathodes, when cycled at a high cut off voltage, can form a P-rich SEI layer on their surface, which is a direct evidence of Li-salt ( $\text{LiPF}_6$ ) decomposition (Figure 1). Our systematical investigations indicate such cathode/Li-salt side reaction shows strong dependence on structure of the cathode materials, operating voltage and temperature, indicating the feasibility of SEI engineering. These findings provide us valuable insights into the complex interface between the high-voltage cathode and the electrolyte. On the other hand, we also investigated the delicate functioning mechanism of  $\text{Al}_2\text{O}_3$  coating layer on  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathode. We discovered that in terms of surface chemical function, the  $\text{Al}_2\text{O}_3$  coating suppresses the side reaction between cathode and the electrolyte upon the battery cycling. At the same time, the  $\text{Al}_2\text{O}_3$  coating layer also eliminates the chemical reduction of Mn from the cathode particle surface, therefore avoiding the dissolution of the reduced Mn into the electrolyte (Figure 2). In terms of structural stability, we found that the  $\text{Al}_2\text{O}_3$  coating layer can mitigate the layer to spinel phase transformation, which otherwise will initiate from the particle surface and propagate towards the interior of the particle with the progression of the battery cycling. The atomic to nanoscale effects of the coating layer

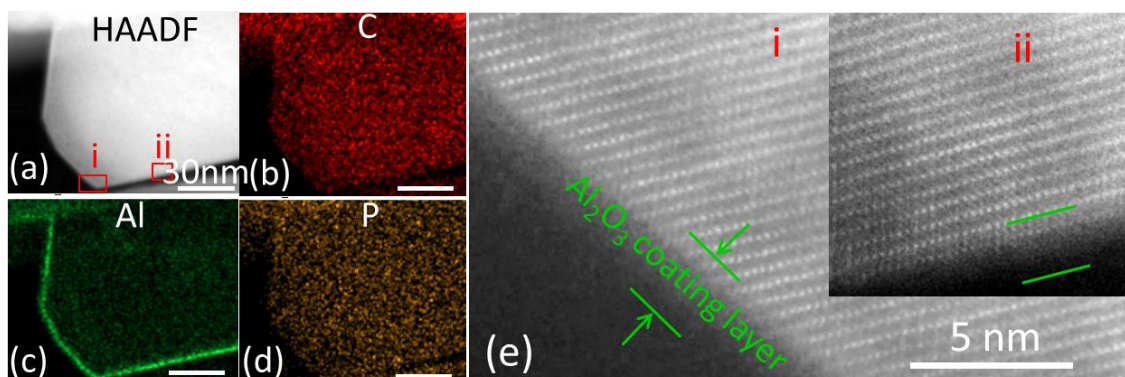
observed here provide insight for optimized design of coating layer on cathode to enhance the battery properties.

#### References:

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**Figure 1.** STEM-EDS mapping on a 40 cycles particle from uncoated electrode. (a) STEM-HAADF image, (b) O map, (c) Ni map, (d) Mn map, (e) C map and (f) P map. (g) high resolution image shows a surface reconstruction layer (SRL) formed after 40 cycles.



**Figure 2.** STEM-EDS maps and high resolution STEM-HAADF images of a particle with alumina coating layer after 40 cycles. (a) STEM-HAADF image, (b) C map, (c) Al map and (d) P map. (e) Lattice images from particle surfaces in (a).