

STEM Investigation of Structural and Chemical Degradation Mechanisms in Na-Based Batteries

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Meeting-report

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Sadikul Alam¹, Gabriel Calderón Ortiz¹, Jehee Park², Xinwei Jiao³, Junbin Choi³, Jung-Hyun Kim³, Eungje Lee⁴, and Jinwoo Hwang^{1,*}

¹Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, USA

²Department of Chemical and Biological Engineering, Hanbat National University, Yuseong-Gu, Daejeon, Republic of Korea

³Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA

⁴Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA

*Corresponding author: hwang.458@osu.edu

Sodium-ion batteries (SIBs) are increasingly getting more attention as an alternative to lithium ion batteries (LIBs) which are susceptible to supply concerns [1, 2], with ample sodium resources available globally. SIBs offer comparable chemistry and manufacturing to LIBs and potential for higher energy densities [1, 3, 4]. However, achieving an ideal SIB requires addressing the balance of energy density, materials cost, and structural stability, aiming for a low-cost, stable battery (i.e. least phase change, Na⁺ vacancy ordering, oxygen loss, and surface reactions) with high energy density (i.e. more cationic redox reactions, anionic redox reactions, and redox potential) [5].

The cathode material is crucial for SIB efficiency, influencing over 60% of it [6]. Although cathodes undergo fewer volume changes than anodes during cycling, they still experience structural alterations due to sodium ion size. Improving SIB energy density requires cathode materials with ample active sites, robust architectures, and open ion pathways, yet these assumptions lack validation through electrode atomistic characterization [7]. Unique electrode/electrolyte interphases in SIBs impact battery performance by delaying undesirable reactions but studying them faces challenges due to their fragile nature and nanoscale dimensions, limiting our understanding of these interfaces [4].

Our approach aims to study cathode interfaces post charging-discharging cycles, observing atomic arrangements periodically to understand material structure-property relationships. Determining transition metal ionic charges provides precise atomic structure information. Using Scanning Transmission Electron Microscope (STEM) for high-resolution imaging, Electron Dispersive Spectroscopy (EDS) for elemental mapping and Electron Energy Loss Spectroscopy (EELS) for confirming oxidation states, we track structural changes and cathode phase transformations. Clarifying microstructural changes through microscopy will guide battery scientists in stabilizing cathodes through methods like defect engineering, nanostructuring, or composition tuning with specific materials such as AlO₃, WO₃, AlF₃, or ZnO [9].

This study investigates how cycling affects sodium content in the cathode and the role of AlF₃ coating in maintaining structural stability. Various microstructure characterization techniques were used, including diffraction pattern analysis, atom imaging, EDS and EELS mapping and spectrum analysis. Figures 1 and 2 compare the microstructure of cycled and non-cycled Na_{2/3}Ni_{1/3}Mn_{2/3}O₂ cathodes. It is shown that structural degradation occurs after 100 cycles. EELS also indicates that the spatial variation of Na increases in the cycled sample. Pristine samples before and after AlF₃ coating on the surface are shown in Figure 3. The effect of the AlF₃ coating on the structural and chemical damage of the cathode after the cycling will be discussed in this presentation [10].

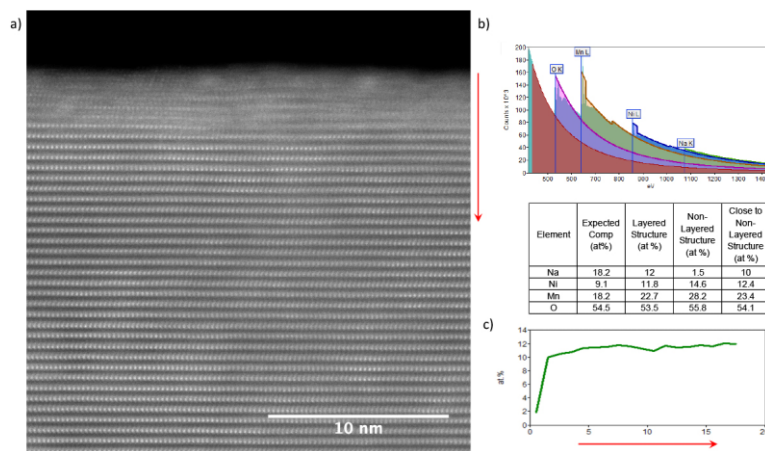


Fig. 1. a) STEM image b) EELS analysis c) Atomic percentage of Sodium while line scanning from top towards bottom as the red arrows show. Image analysis represents pristine cathode of Na_{2/3}Ni_{1/3}Mn_{2/3}O₂.

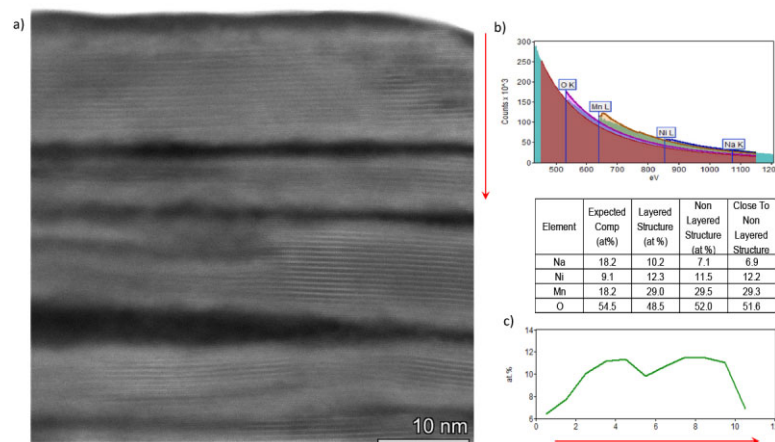


Fig. 2. a) STEM image b) EELS analysis c) Atomic percentage of Sodium while line scanning from top towards bottom as the red arrows show. Image analysis represents 100th Cycled cathode of Na_{2/3}Ni_{1/3}Mn_{2/3}O₂.

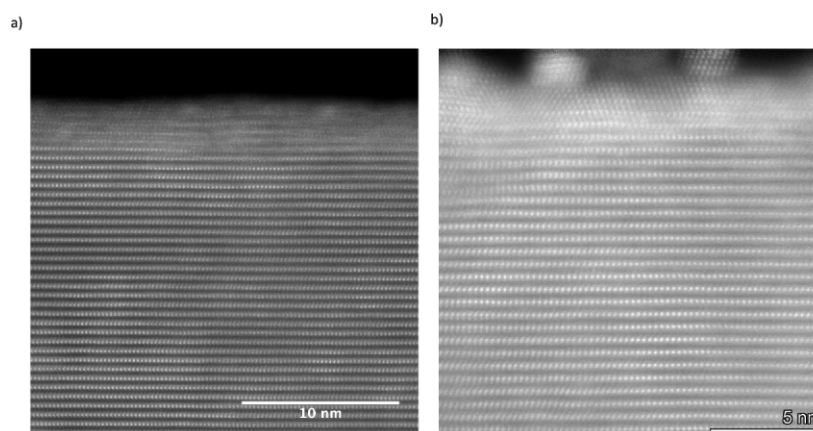


Fig. 3. High resolution image of a) Pristine and b) AlF₃ coated Na_{2/3}Ni_{1/3}Mn_{2/3}O₂.

References

1. Zhang, W., *et al.*, *EnergyChem*, 2019. 1(2).
2. Nurohmah, A.R., *et al.*, *Materials for Renewable and Sustainable Energy*, 2022. 11(1): p. 71-89.
3. Nayak, P.K., *et al.*, *Angew Chem Int Ed Engl*, 2018. 57(1): p. 102-120.
4. Song, J., *et al.*, *Advanced Energy Materials*, 2018. 8(17).
5. Wang, K., *et al.*, *Advanced Functional Materials*, 2023. 33(13).
6. Li, Y., *et al.*, *Advanced Energy Materials*, 2020. 10(27).
7. Hwang, J.Y., *et al.*, *Chem Soc Rev*, 2017. 46(12): p. 3529-3614.
8. Gong, D., *et al.*, *Small Science*, 2021. 1(6).
9. Chen, J., *et al.*, *Energy & Environmental Materials* 6 (2023).
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