Operando XRD and TXM-XANES Reveal Dynamic Cation Disorder in Co-Mn-Al Spinel as the Key Mechanism for High-Performance Li-S Batteries

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Spinel oxides are promising catalysts for lithium-sulfur (Li-S) batteries [1-2], yet the link between their structural dynamics and catalytic function under extreme conditions remains elusive. Here, we employ a multimodal synchrotron approach to unravel the redox and structural evolution of a partially inverted $Co_2Mn_{0.5}Al_{0.5}O_4$ (CMA) spinel. Through operando X-ray diffraction (XRD), nanoscale transmission X-ray microscopy with XANES mapping (TXM-XANES), and extended X-ray absorption fine structure (EXAFS), we reveal a reversible, redox-driven redistribution of Co^{2+}/Co^{3+} and Mn^{3+}/Mn^{4+} between tetrahedral and octahedral sites. This dynamic cation disorder facilitates moderate lattice contraction while preserving long-range order, even after 400 cycles at a high 10C rate. Figure 1a shows the operando XRD evolution of the (311) reflection during the first cycle. The lattice parameter expands by +0.045% upon discharge (Q minimum at 1.7V, Li_2S formation) and partially recovers upon charging, indicating reversible lithiation of the spinel framework (Δa = +0.001485 Å). The peak broadening (δQ) correlates with heterogeneous surface lithiation and polysulfide adsorption, confirming CMA's dynamic interaction with lithium polysulfides (LiPSs). TXM-XANES imaging (Figure 1b) directly visualizes an increase in Co^{2+} content and its spatial localization at particle edges post-cycling, confirming its active role in polysulfide mediation. Linear combination fitting reveals a decrease of $Co^{2.67+}$ amounts from 73.4% to 52.6% and a corresponding increase in Co^{2+} from 26.5% to 47.3% after 400 cycles. The formation of Co-S and Co-O-S interfacial domains, driven by crystal-field effects and spin-state transitions, is identified as the origin of enhanced catalytic activity. Density functional theory (DFT) calculations corroborate strong polysulfide adsorption (E_ad_s= -5.93 to -8.19 eV) and charge transfer via *p-d* hybridization. In situ annealing XRD (Figure 1c) reveals that the partially inverted structure emerges at ~890°C, with nano-segregated phases reincorporating upon cooling, confirming that controlled cation disorder is an intrinsic feature of CMA synthesis. These findings establish dynamic cation disorder as a fundamental design principle for spinels, enabling them to act as robust, bifunctional catalysts that ensure both long life and high power in Li-S batteries.

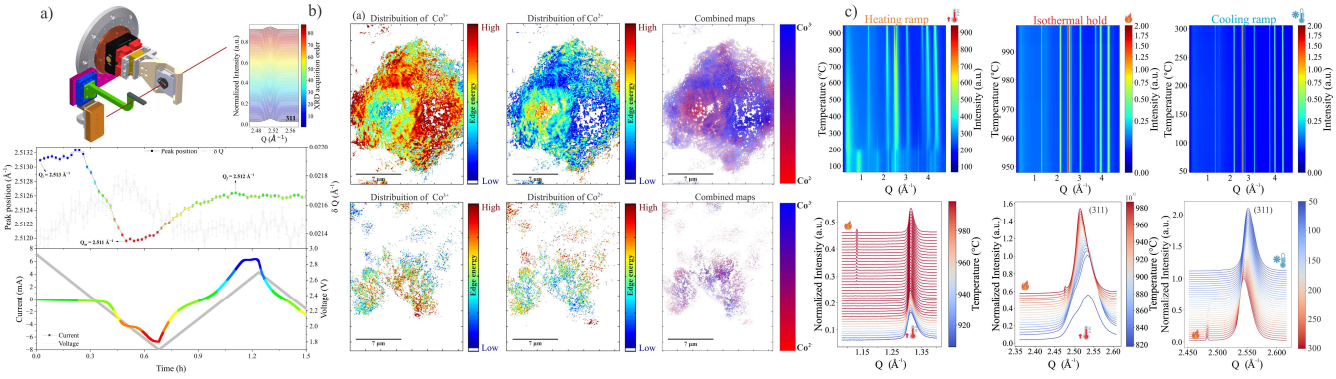


Figure 1. *(a) Operando XRD evolution of the CMA (311) reflection during the first cycle, showing lattice expansion upon discharge (Li_2S formation) and contraction upon charge. (b) TXM-XANES chemical maps of Co oxidation states in pristine (top) and cycled (bottom) electrodes after 400 cycles at 10C, revealing Co^{2+} enrichment at particle edges. (c) In situ annealing XRD showing the emergence of the partially inverted spinel structure at ~890°C, with nano-segregated phases (arrows) reincorporating upon cooling.*

[1] É.A. Santos et al., Nano Energy 116 (2023) 108809.
[2] É.A. Santos et al., Nano Energy 130 (2024) 110098.

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