Interpretable Machine Learning Framework: Unveiling Redox Mechanisms in Lithium-Rich Layered Cathodes

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Abstract

The increasing global demand for sustainable energy storage solutions has underscored the critical role of lithium-ion batteries in advancing modern energy technologies.[1] Among various cathode materials, lithium-rich layered oxides (LRLOs) have emerged as one of the most promising candidates due to their high theoretical energy density, driven by dual cation-anion redox processes, and the economic advantages of using primarily earth-abundant manganese.[2-4] These materials, however, face significant challenges such as voltage fade, capacity degradation, and structural instability during prolonged cycling.[5, 6] These issues arise from their intricate electrochemical behavior and inherent material complexities, posing substantial obstacles to their commercialization. Resolving these challenges necessitates a thorough understanding of the degradation mechanisms and pathways that limit their performance.

In this study, we present a novel data-driven framework to tackle these challenges. By leveraging unsupervised machine learning techniques, particularly Principal Component Analysis (PCA), we developed a systematic approach to analyze extensive experimental datasets. The framework was applied to more than 30,000 charge curves collected under consistent conditions from LRLO coin cells. This methodology offers a detailed understanding of the key electrochemical features influencing material behavior. By isolating and analyzing the principal components, we successfully disentangled overlapping oxygen and manganese redox reactions, thereby providing critical insights into the performance and degradation of LRLOs.

The analysis revealed the physical significance of the two principal components, PC1 and PC2. PC1 primarily captures kinetic properties, such as cell resistance, which suppress oxygen redox reactions. PC2, on the other hand, reflects manganese reduction and the ratio of cation and anion redox reaction. These insights were instrumental in elucidating the degradation mechanisms of LRLOs. Through this analysis, we identified a typical degradation pathway: PC2 increases initially, followed by a rise in PC1. This sequence suggests that manganese reduction dominates the early degradation stages, while resistance increases become prominent in the later stages. The ability to interpret the relationship between PC1 and PC2 offers a systematic way to understand and mitigate performance loss.

In addition to the typical degradation pathway, the PCA framework enabled us to identify and characterize alternative degradation pathways. Deviations from the typical pathway were analyzed, revealing subtle differences in how material compositions and synthesis methods affect degradation. This comprehensive diagnostic capability enhances our understanding of LRLO behavior under various conditions and facilitates the development of tailored strategies to address specific performance issues.

The predictive power of the PCA framework further underscores its utility. By using partial voltage data, the model accurately reconstructed complete charge curves with minimal error. Even when applied to new datasets not included in the training phase, the model maintained high accuracy, achieving a root mean squared error (RMSE) of less than 0.4 mAh/g. This level of predictive accuracy is particularly valuable for rapidly screening and optimizing LRLO compositions and synthesis methods. Moreover, the ability to generalize to new datasets highlights the robustness of the framework in real-world applications.

One of the key strengths of the proposed framework lies in its robustness and adaptability. The generalization ability of the PCA model was validated by comparing PC1-PC2 plots of test datasets with those of training datasets. Despite variations in material compositions and experimental conditions, the reconstruction accuracy of the test set closely matched that of the training set. Additionally, the model demonstrated the capacity to identify outlier scenarios characterized by significant deviations in PC1 and PC2 values. These outliers, associated with phase separation and severe degradation, were confirmed through complementary XRD analyses. Importantly, the inclusion of outlier data in the training set did not alter the structure of the principal components, demonstrating the resilience of the model. This characteristic eliminates the need for frequent retraining and ensures sustained performance, making the framework particularly suited for dynamic research environments.

The interpretability of the PCA framework also plays a crucial role in its practical application. By connecting principal components to physical properties such as resistance and redox activity, researchers can gain actionable insights into the interplay between structural evolution and electrochemical behavior. For instance, PC1 trends can inform strategies to mitigate resistance growth, while PC2 patterns offer clues for stabilizing manganese redox reactions. Such insights are

essential for guiding the rational design of LRLO materials with enhanced performance and stability.

In conclusion, this study introduces a transformative approach to addressing the critical challenges associated with LRLO development. By combining data-driven methodologies with domain expertise, we have provided new insights into the degradation mechanisms and pathways of these promising cathode materials. The proposed framework not only advances the understanding of LRLO electrochemical behavior but also paves the way for the design of next-generation lithium-ion batteries with superior stability and energy density. Additionally, the versatility of this framework suggests its applicability to other battery chemistries and energy storage technologies, contributing to the broader development of sustainable energy solutions.

References

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Figures

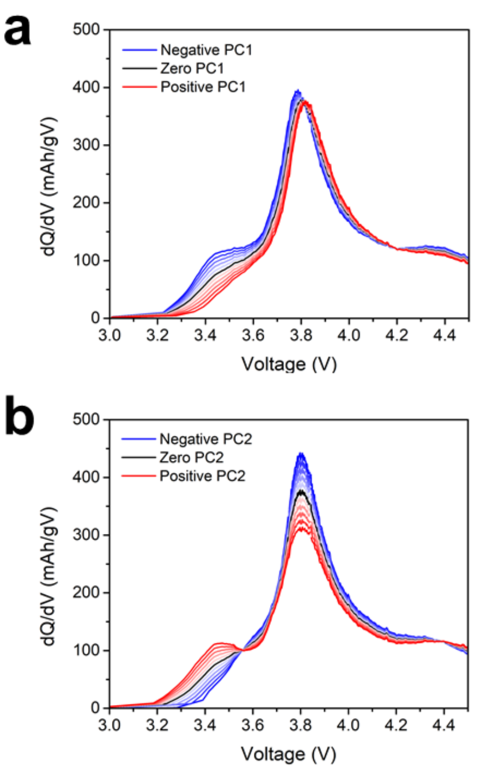

Figure 1. dQ/dV curves as influenced by (a) PC1 and (b) PC2.

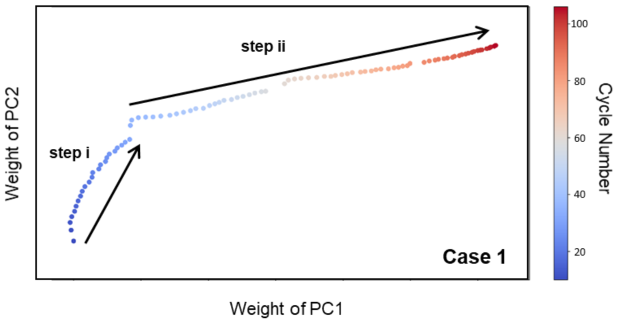

Figure 2. Relationship between characteristic cycle behavior and weights of the PC1 and PC2, divided into two distinct phases.

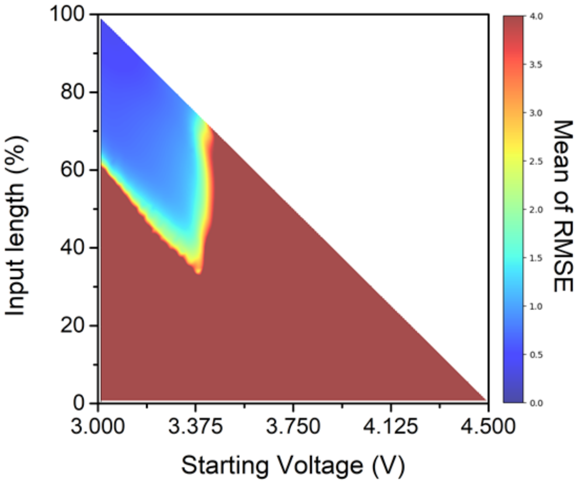

Figure 3. Average prediction error over the charge curve.