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Machine-Learning-Enabled Robust Phase Mapping from X-ray Hyperspectral Imaging of Cycled Sodium-Ion Cathodes

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Understanding how electrochemical cycling affects the local structure and chemistry of battery electrodes requires techniques that can resolve nanoscale phase changes [1]. During charging and discharging, ions move in and out of the electrode, causing local structural rearrangements and often leading to the coexistence of multiple phases with different electrochemical behaviors. This multiphase nature creates strong spatial heterogeneity and complex transformation pathways, which directly influence reaction kinetics, reversibility, and long-term stability [2]. Accurately mapping these coexisting phases and their distribution is therefore essential for designing and optimizing advanced battery materials. Scanning transmission X-ray microscopy (STXM) is particularly well suited for this task, as it combines nanometer-scale spatial resolution with hyperspectral imaging, capturing an X-ray absorption spectrum of a core-level excitation (e.g., K, L, M edges…) at each scanning point. STXM has proven especially effective for tracking phase evolution and compositional variations in battery electrodes. However, to limit radiation damage and reduce acquisition time, STXM measurements often use sparse energy sampling, which can make it challenging to distinguish phases with subtle spectral differences.

In this study, we focus on the sodium-ion battery cathode material $Na_3V_2(PO_4)2F_3$ (NVPF), a promising candidate for sodium-ion batteries due to its high operating voltage and structural stability [3]. Previous work has shown that NVPF undergoes a complex, multi-step desodiation process, involving several intermediate phases and significant lattice distortions [4]. To investigate this behavior, NVPF samples were electrochemically prepared to reach different states of charge $Na_{2.5}$VPF, Na_2VPF, Na_1VPF, and $Na_{0.6}$VPF were analyzed using STXM-XANES, providing spatially resolved insight into vanadium redox chemistry during electrochemical cycling. To address the challenges posed by sparse spectral sampling, we developed a Python-based data analysis workflow that combines similarity metrics with machine learning techniques [5]. Spectral similarity between experimental data and reference spectra was quantified using the Pearson correlation coefficient. Phase and reliability maps generated from this analysis are shown in Figures 1a-b, while Figures 1c-g display correlation maps for each NVPF phase, highlighting spatial variations of the correlation coefficient relative to reference spectra. Regions of ambiguity in the phase maps, where correlation coefficients between two phases were nearly identical (≤ 0.005), were further resolved using a Gaussian mixture variational autoencoder (GMVAE) [6]. By projecting ambiguous pixels into a low-dimensional latent space optimized for phase discrimination, each pixel was assigned to the closest phase distribution using the Mahalanobis distance, resulting in the final phase map shown in Figure 2c. Figures 2d-f illustrate the corresponding phase distributions in latent space before and after ambiguity resolution, demonstrating how the GMVAE probabilistically separates ambiguous phases and increases confidence in phase assignment.

Applying this combined correlation and GMVAE-based approach to NVPF particles with different sodium content reveals pronounced nanoscale heterogeneity during desodiation. Intermediate states of charge exhibit the coexistence of multiple sodium phases within individual particles, with different regions transforming at markedly different rates. This behavior is consistent with previously observed non-uniform reaction pathways in battery nanoparticles [2]. Overall, these results suggest that NVPF desodiation proceeds via a spatially heterogeneous, multi-step mechanism governed by local structural and kinetic factors. This study also demonstrates that machine learning assisted analysis can be effectively integrated with hyperspectral X-ray microscopy to extract reliable chemical and structural information from complex, sparsely sampled datasets. The methodology is versatile and can be applied to other energy materials and spectro-microscopy techniques like electron energy-loss spectroscopy (EELS).

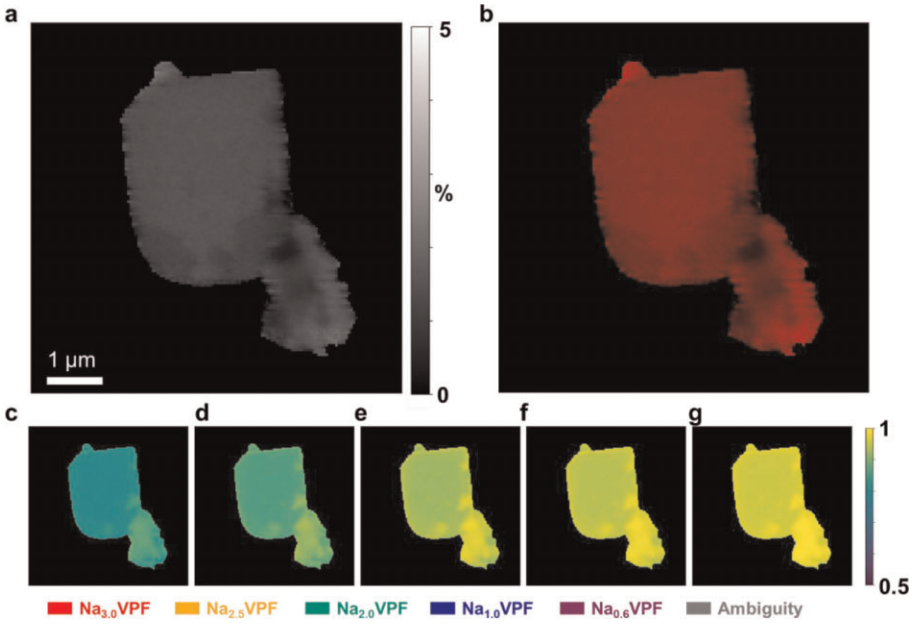

Fig. 1: Correlation and reliability mapping of $Na_3V_2(PO_4)2F_3$ (NVPF). (a) Reliability maps derived from Pearson correlation analysis(b) Combined phase and reliability map (c–g) Pearson correlation maps for $Na_3V_2(PO_4)2F_3$ at different sodium contents $Na_xV_2(PO_4)2F_3$ (x=3.0,2.5,2.0,1.0,0.6).

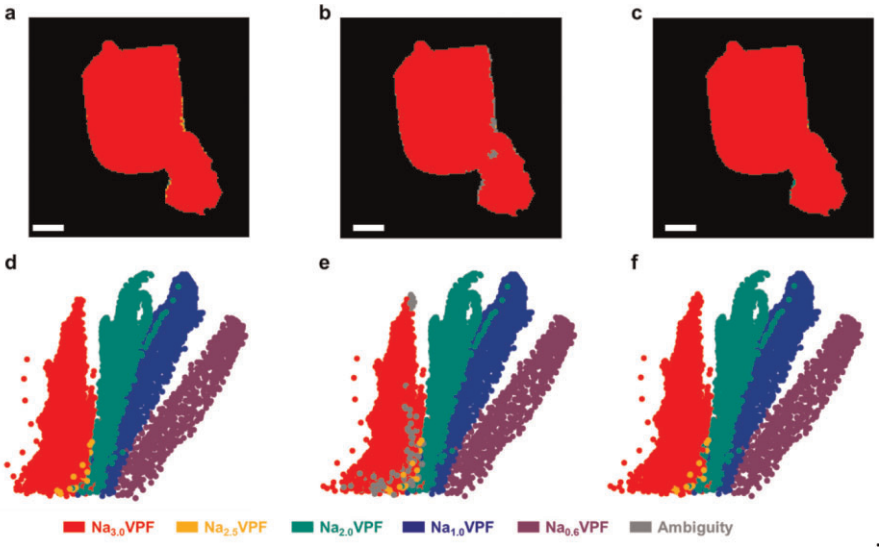

Fig. 2: Phase mapping of a $Na_xV_2(PO_4)2F_3$ sample. (a) Initial phase map obtained using Pearson correlation analysis. (b) Ambiguity map (c) Final phase map after resolving ambiguous regions using a Gaussian Mixture Variational Autoencoder (GMVAE) (d) Phase distributions in the GMVAE latent space before projecting ambiguous pixels. (e) Projection of ambiguous pixels into the latent space (grey). (f) Latent space after resolving ambiguous pixels.

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