Machine learning classification of oxidation states in strontium iron oxide based on electron energy loss spectra

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Abstract
Stochiometric evolution in strontium iron oxide is of critical importance to the understanding of process-structure-property relationship of the material. In-situ electron energy loss spectroscopy (EELS) can be used to reveal the changes in oxidation states during the annealing process, whereby the precise spatial information of oxidation transition may be determined. However, observing stochiometric changes in the material at real-time poses challenge due to the large amount of noisy data. Machine learning methods demonstrate promise in both improving signal interpretation and automating precise control of strontium iron oxide synthesis. This paper highlights and compares the use of various deep learning architectures, both supervised and unsupervised, in classifying the oxidation states from temporal EELS data.

Introduction
Strontium iron oxide, $SrFeO_{3-\delta}$ or SFO, is a magnetic material commonly known for its high coercivity with applications ranging from DVDs to electric motors [1]. However, a small change in its oxide composition to δ=0.125 brings about a metal-to-insulator transition. This variation causes a large change in resistivity, whereby the reduction and oxidation mechanism of SFO can be utilized in a new generation of transistors [2,3]. At δ=0.25, the crystallographic structure becomes orthorhombic, and this coincides with an antiferromagnetic transition which may find potentials in novel applications such as spintronics or antiferromagnetic memories [4]. From these examples, it becomes apparent that the stoichiometric information of SFO can serve as an efficient tool in tuning the electronic, crystallographic and magnetic states during material processing.

To monitor the stoichiometry of SFO, electron energy loss spectroscopy (EELS) can be utilized. EELS is a high-speed characterization technique that can be used to obtain structural and chemical information about a material by measuring material's interaction with electron beam. EELS is also a spatially localized technique where the measurement resolutions can be achieved to ~0.1 nm. Therefore, implementing EELS as an in-situ characterization tool during oxidation-reduction or annealing processes can help reveal how various phases of SFO grows in real time. However, determining the chemical composition at nanoscale using EELS can face challenges due to the low signal-to-noise ratio (SNR). While this problem can be mitigated by summing up the signals over a large area or increasing the time of signal collection, high spatial resolution and fast measurement are needed to monitor the evolution of SFO at real time.

From Nvidia's acoustic suppression to Google's image recognition [5], machine learning algorithms have proven useful as a noise reduction and classification techniques in various applications. In this paper, we explore the use of machine learning models and deep learning architectures in both supervised and non-supervised manner to classify oxidation states of strontium iron oxide.

Materials Data
To construct a test dataset, we collected the EELS spectra from an SFO sample under transmission electron microscope (TEM). Ten EELS spectrum images of size 30-by-300 pixels were collected sequentially over the same area. The sample was then ex-situ annealed to drive reduction reaction before additional 10 images were collected to observe the spectral differences. In total, 180,000 spectra were collected with 3710 energy channels, 0.125 eV per channel, and the energy field of view extending from 387.5 eV to 851.25 eV.

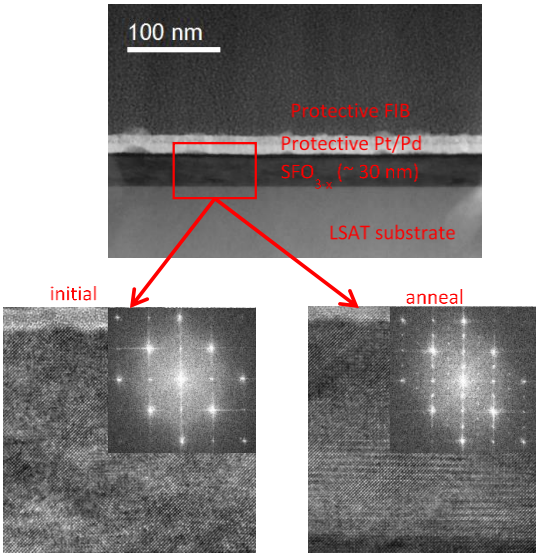

Figure 1. The top image is a dark field image of the cross-sectional structure of the sample. The two lower images show the lattice structure and diffraction pattern of the sample before and after annealing.

High-resolution transmission electron microscopy (HRTEM) was then used to confirm the crystal structure before and after annealing. The analysis shows that the sample contains the perovskite structure before annealing and the orthorhombic structure after annealing.

These correspond with the crystal structures of $SrFeO_3$ and $SrFeO_{2.5}$, respectively. We confirmed this transition by observing the changes in EELS spectrum fingerprint. By averaging individual spectra from the annealed and non-annealed samples, we obtained a high SNR that displayed apparent changes at 525-550 eV and 710-730 eV. These coincide with the oxygen K-edge and ferrite L-edge energy values, thus confirming the change in chemical composition of SFO after annealing.

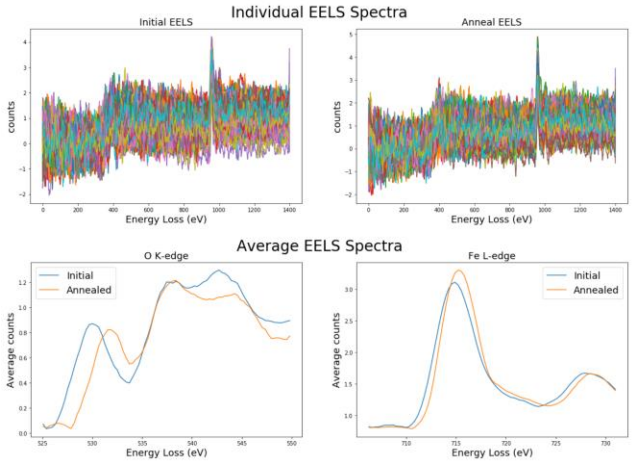

Figure 2. Top two graphs show the individual spectra from each pixel on the EELS image. The high signal-to-noise ratio (bottom) is obtained by averaging the spectra in each EELS image.

Data Processing

Before the collected data can be used to train machine learning models, a number of feature engineering steps was completed to ensure that the data was in a correct format and can be properly utilized.

(a) Background Calibration: Due to an issue with the EELS collection software, the data must first be corrected by adding a dark reference spectrum to each individual collected spectrum. By the nature of EELS data, all spectra also have an exponential background noise that can be corrected by performing power-law curve fit.

(b) Reducing random noise: To allow the machine learning models to focus on the trends of the signal, Savitzky–Golay filter was applied to smooth out the local variations in the EELS spectra [6].

(c) Down-sampling: Training deep learning models on complex EELS signals can be computationally expensive. Reducing the number of data points, while maintaining the important features of the spectra, will help to reduce computational requirement and allow faster training time.

(d) Normalization: This process is important in ensuring that every spectrum is in the same numerical scale and that no outliers will dominate the training set. Normalization will therefore eliminate biases in spectral domain.

(e) Region of interest (ROI): The large number of energy loss levels, most of which are not of interest, training machine learning models can require a large number of parameters, thus computationally expensive. For the purpose of this study, only the energy range at O K-edge (81 channels) was used for spectra classification.

Models and Discussion

In this study, we compare various machine learning methods in classifying oxidation state of SFO using the anneal and non-anneal dataset. The three core models covered include Support Vector Classification (SVC) and Convolutional Neural Network (CNN) which were performed as a supervised learning task, and lastly is the Recurrent Neural Network (RNN) Autoencoder which was utilized as an unsupervised learning task.

(a) Supervised Machine Learning

(a.1) Support Vector Classification (SVC)

SVC is a classifier that aims to find a hyperplane to best separate the data. However, by itself, SVC does not perform well when there is a low SNR. For this reason, we performed SVC in conjunction with dimensionality reduction techniques, namely principle component analysis (PCA), t-distributed stochastic neighbor embedding (t-SNE), and Independent Component Analysis (ICA). By extracting the principle factors that best describe the data, SVC will be more effective.

(a.1.1) Principal Component Analysis (PCA)

Intuitively, scientists classify the oxidation state by looking at the differences in the shape of the peak. Mathematically, these differences are the variances in data that have the underlining physical meaning. PCA is a dimensionality reduction technique used to emphasize these variations in signals and extract the major patterns in a dataset. As shown in figure 3, the colors yellow and purple indicate the oxidation states of each spectrum corresponding to component 1 and 2. However, the classification of two oxidation states using 2-component PCA in this case will prove difficult as these two principal components only explain 48% of the overall variance as shown in figure 4. In order to explain 90% of the data, we need to consider at least 8 PCA components.

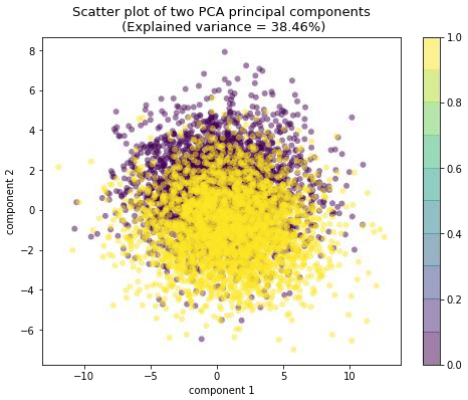

Figure 3. The combination of two PCA components is not linearly separable; thus, it is not a good method to classify the spectra.

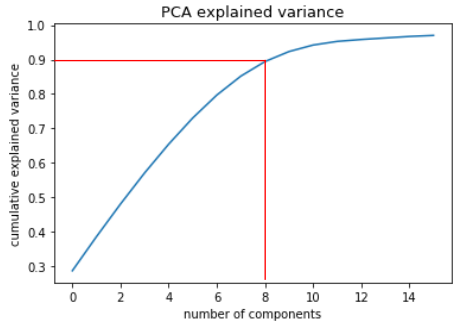

Figure 4. Cumulative explained variance measures the proportion of variances that is counted for by the trained PCA model.

To incorporate these variances, we applied on a 16-component PCA model to better classify the oxidation states. Figure 5 shows the 70.05% prediction accuracy after using 80:20 train-test split. We have also evident the increase in accuracy with the increase number of training dataset.

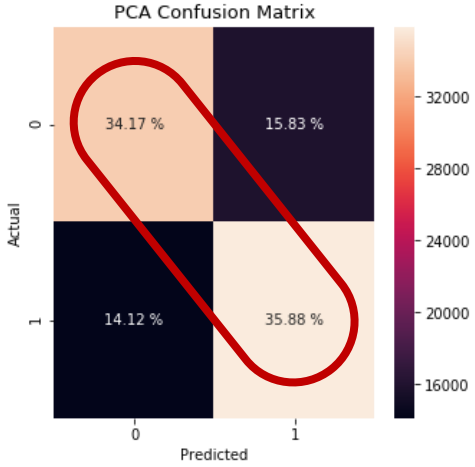

Figure 5. Confusion matrix of the prediction with PCA+SVC model

(a.1.2) t-Distributed Stochastic Neighbor Embedding (t-SNE)
While PCA looks at the variance of the entire dataspace, t-SNE looks at the local variances in the manifold. In other words, t-SNE explores how the data is arranged in a high-dimensional space [7]. The prediction accuracy using t-SNE with PCA proved to be worse than that with PCA. It must also be noted that with the same amount of training dataset, t-SNE took significantly more time to both train and predict. In the real-time operation, t-SNE will not be applicable for in-situ analysis.

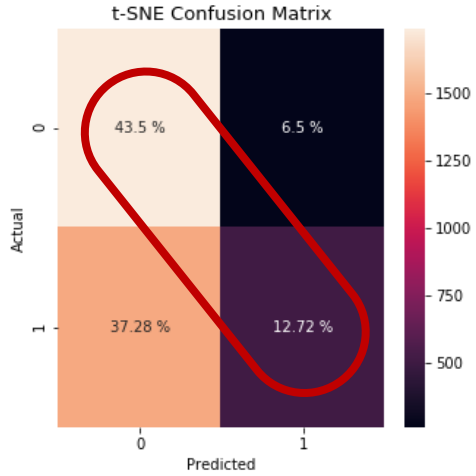

Figure 6. Confusion matrix of prediction with t-SNE+SVC model

(a.1.3) Independent Component Analysis (ICA)
In contrast to the PCA, ICA does not choose components based on greatest variance but based on the strongest independent signals [8]. This technique assumes that every signal is the combination of various independent sources. With a 16-component ICA, the SVC model was able to achieve the accuracy of 69.93%, slightly slower than PCA+SVC.

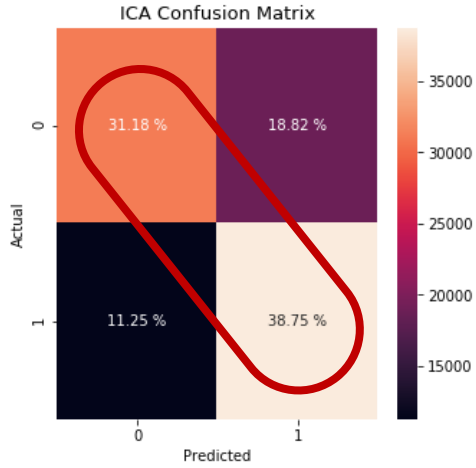

Figure 7. Confusion matrix of the prediction with ICA+SVC model

(a.2) Convolutional Neural Network (CNN)
Another approach to classifying spectra is by the use of one-dimensional CNN. 1-D CNN works as a biased filter which finds a set of sequential patterns that are most prominent across all spectra. The model consisted of two 1D convolutional layers, max pooling, and two fully connected layers with rectified linear units (ReLu) as activating functions. This resulted in 86% prediction accuracy as shown in figure 8. This is considered much better accuracy compared to other SVC combinations.

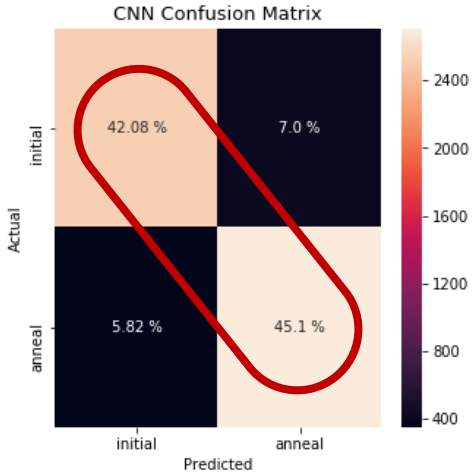

Figure 8. Confusion matrix of the prediction using CNN model.

(b) Unsupervised Machine Learning

Two of the major limitations of supervised machine learning method remain that (1) the trained data given is binary, while the actual material system may contain oxidation states that can be anywhere between δ=0 and δ=0.5, and (2) the model only works for datasets that are collected using the same settings e.g. SVC and CNN models will not work with different sampling rate or the instruments with different noise characteristics. For these reasons, developing the unsupervised machine learning model could prove to be of significant value.

(b.1) Recurrent Neural Network (RNN) Autoencoder

One deep learning architecture that can be applied is RNN, which is particularly helpful when dealing with temporal data. In this case, the energy loss spectra domain was used as the temporal steps. The model will then analyze the entire energy sequence using the long short-term memory (LSTM). As LSTM is trained with various spectra, it attempts to remember the past temporal knowledge that are most relevant and forgets those that are least relevant [9].

In particular, we trained RNN with an autoencoder architecture. An autoencoder encodes the input data into lower dimensional layers and attempts to reconstruct the original signal. In this way, the architecture seeks for the most relevant information in the spectra to keep. Figure 9 shows how an autoencoder represents each random spectrum at a low dimensional layer. As can be seen, the model closely traced along the general trend of the curve and ignored smaller features that may be deemed as noise.

In this model, we constructed a low dimensional layer of 9 neurons. Reconstructing the low dimensional layer back into spectral images also poses an opportunity to see the changes of spectra, thus oxidation states, in real time. While the variation of reconstruction in figure 10 can be difficult to distinguish, figure 11 shows the sum of intensity in the low dimensional neurons. Therefore, we should be able to expect a lower activation at neurons 2 and 3 for non-annealed spectra.

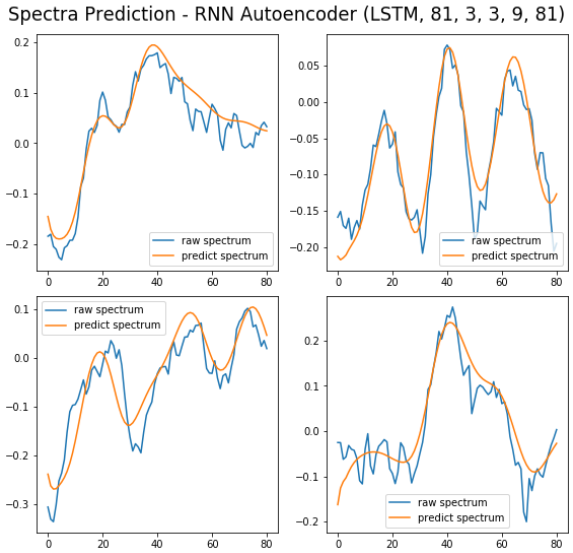

Figure 9. Visualization of the predicted spectrum using the low dimensional layer.

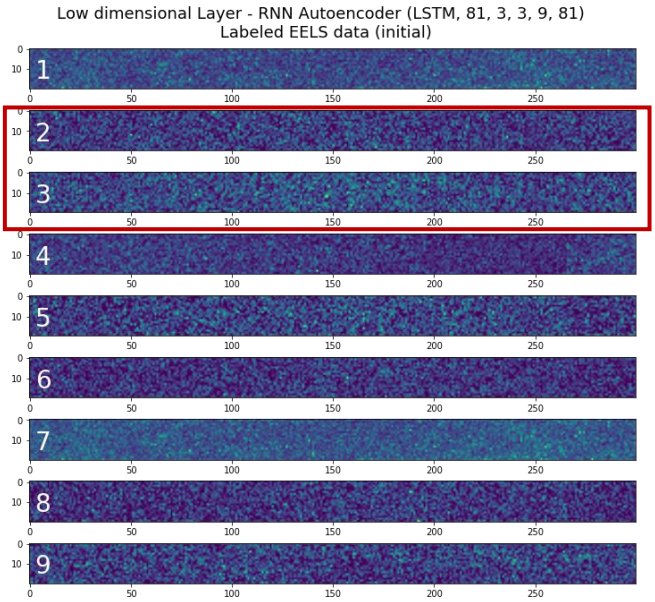

Figure 10. The reconstruction of low dimensional layer into a 30x300 pixel EELS spectral image. The red rectangle signifies the neurons that are expected to look dimmer for annealed spectra.

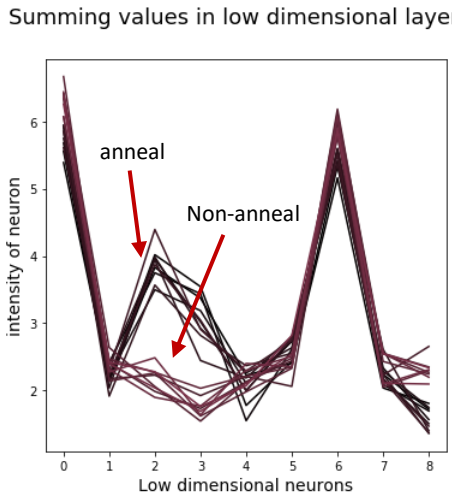

Figure 11. Variation of intensity in low dimensional neurons in response to the annealed and non-annealed spectra

Conclusion

Machine learning methods are shown to be effective at classifying EELS spectral data. PCA and ICA can help reducing the noise and enabled effective SVC method. Overall, CNN was shown as the best architecture in determining the spectra in a supervised manner. However, the challenges in using supervised machine are the lack of flexibility with the data collection methods and the number of learned oxidation states. The unsupervised learning method, such as RNN Autoencoder, shows potential in tackling the two major issues with supervised learning. Nevertheless, the major challenge in using RNN Autoencoder for classifying oxidation state is in reducing spectral noise. Further investigation is needed.

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