

Applications Note

High-throughput XPS Analysis of Na-Fe-Mn-O Cathodes for Na-ion Batteries

MO495(A)

Keywords Battery, combinatorial analysis, XPS, oxidation states.

Overview

This applications note highlights materials characterisation of sodium-based cathodic materials studied using high-throughput X-ray photoelectron spectroscopy.

Introduction

The battery plays a pivotal role in the storage, transfer, release, and usage of electric energy. With the wide application of lithium batteries and the huge demand for electric vehicles and large-scale energy storage, there are more and more concerns about the sustainability of Li-ion batteries.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. Among them, sodium layered oxides are very important cathode materials with good sodium mobility and high specific capacity. Layered transition metal oxides Na_xMeO_2 consist of layers of MeO_6 octahedra to preserve 2D transport channels for direct Na ion diffusion. For metal selections, Me can be Fe, Mn, Co, Cr, Ni, Ti, V and their combinations. Interestingly, single transition metal oxides show worse battery performance than binary or ternary

transition metal systems, making composition studies imperative. Metal combinations can achieve tuneable properties with structure, electrochemical performance, and cycling stability. However, to date, the battery performance has not been competitive, and promising Na-Fe-Mn-O (NFMO) materials have been plagued by poor stability in air.

Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation.

This represents a first ever systematic study of a ternary system for Na-ion cathodes and demonstrates that tuning the material's composition can have a dramatic impact on air stability, even without the addition of new elements.

Experimental

Twenty one powder samples were mounted on a single AXIS Nova sample platen. Total analysis time for all sample spectra acquired was <7 hours.

Automated background and constrained peak fitting was applied to all spectra to ensure systematic analysis with no manual input bias.

Results and Discussion

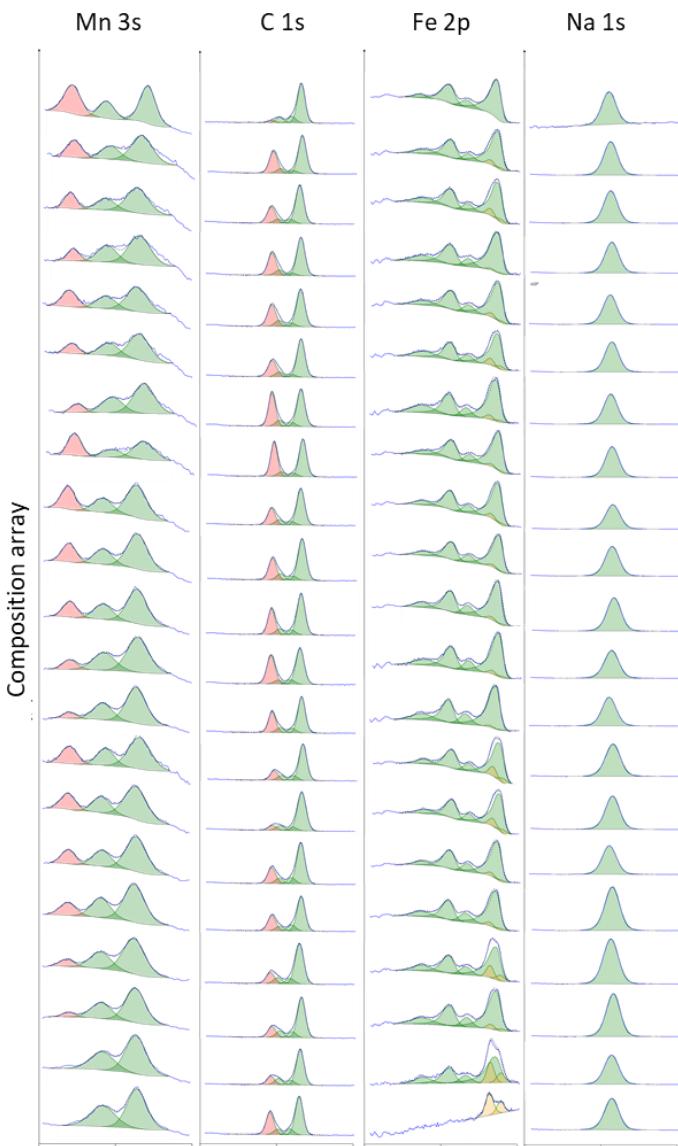


Figure 1: XPS spectra Mn 3s, C 1s, Fe 2p and Na 1s (left to right)

Fast chemical state analysis XPS was performed for all 21 compositions (figure 1). All spectra are normalised to the same signal intensity.

Manganese:

For manganese, the Mn 3s peak is a useful indicator of the oxidation state of Mn. As described in the literature, there is a linear relation between the Mn valence and the Mn 3s exchange splitting energy [1]. This method of oxidation state analysis is

much simpler to use than fitting the Mn 2p where precise binding energies of oxidation states vary wildly in the literature. For all samples with the ternary matrix, a split of 4.4- 4.6eV was observed corresponding to an oxidation state of +4.

Iron:

Iron is a classic case of XPS “headache” when trying to determine the oxidation states. Bagus, Brundle and Crist illustrate the complexity of the Fe 2p line shape in their recent *ab initio* model of the core line [2]. The peak position for the Fe 2p peak is a good indicator of the oxidation state but there is large variability depending on the bonding environment and matrix pair elements. For +2 species the $\text{Fe}2\text{p}_{5/2}$ peak binding energy can vary from 708.0eV to 711.5eV. For +3 species the energy range is 710.3eV up to 715.1eV — there is considerable overlap in the energy ranges. Previous papers by Biesinger and Grosvenor [3,4] illustrate sensible approaches to the problem but still require confident fitting and sensible background subtraction.

For this sample set we applied a simple logic — combining both the peak position of the $\text{Fe}2\text{p}_{5/2}$ peak and the energy separation between the $\text{Fe}2\text{p}_{5/2}$ peak and the corresponding shake-up satellite. A single asymmetric component was fitted to the primary line to determine the peak position and another symmetric component for the shake-up satellite. The $\text{Fe}2\text{p}_{5/2}$ peak was $710.5 \pm 0.15\text{eV}$ in all cases and the shake up ΔeV was $8.4\text{eV} \pm 0.1\text{eV}$. The combination of both pieces of information leads us to confidently determine the oxidation state of Fe in these samples to be +3 since no +2 oxidation state materials will satisfy both criteria of peak position *and* shake-up energy separation.

Sodium and Carbon:

Generally speaking, 1s line shapes are much simpler to peak fit. For C 1s a high binding energy peak (>289.5eV) was observed for all of the samples. This can be ascribed to the presence of carbonates on the surface. All air exposed samples have this character to a small degree due to the presence of adventitious carbon on the surface — short chained air borne polymer chains. The ratio of carbonate to C-C peaks is consistent across all air exposed samples, the carbonate is typically 5% of the C-C peak. In several of the materials analysed here the carbonate peak is considerably larger than can be attributed to adventitious carbon. This implies the carbonate is formed from reactivity with the air by the species present.

Interestingly the amount of carbonate varies with excess sodium. This indicates the migration of Na and the formation of carbonate varies significantly across the sample set, shown in figure 2 over page.

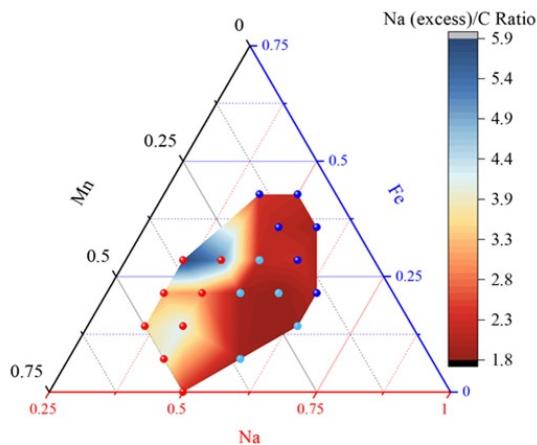


Figure 2: Relationship between Na concentration and carbonate formation (a value of 2 represents Na_2CO_3).

The migration of sodium varies significantly and is a good indicator of long-term material stability. Understanding the correlation of carbonate concentration and excess sodium was possible because we used a large material dataset and looked for trends in material relationships.

The high throughput capability of the AXIS Nova is exemplified by the excellent sensitivity of the instrument—illustrated by the fast analysis times—and the large sample platens accommodate a large number of samples limiting pump down times.

Conclusions

Here we illustrate the importance of high sensitivity for a high-throughput X-ray photoelectron spectrometer. Spectra were acquired quickly with excellent signal-to-noise allowing accurate background subtraction and subsequent curve fitting. Optimised data handling for large datasets allows correlative analysis and determination of chemical states from peak positions.

We were able to identify the oxidation states of the metals present in the ternary matrices and with this combinatorial approach we were able to demonstrate relationships between composition and stability.

For further detailed discussion and supporting information the original peer-reviewed article is available:

Journal of Materials Chemistry A

High-throughput design of Na–Fe–Mn–O cathodes for Na-ion batteries [5]

Acknowledgements

Many thanks to Prof. Eric McCalla and Dr. Shipeng Jia for samples, discussion, thoughts and insight.

References

- [1] V. R. Galakhov, M. Demeter, S. Bartkowski, M. Neumann, N. A. Ovechkina, E. Z. Kurmaev, N. I. Lobachevskaya, Y. M. Mukowskii, J. Mitchell, and D. L. Ederer, Phys. Rev. B 65, 113102 2002.
- [2] P. Bagus *et al.*, Phys. Chem. Chem. Phys., 2022, 24, 4562–4575
- [3] A. Grosvenor *et al.*, Surf. Interface Anal. 2004; 36: 1564–1574
- [4] M. Beisinger *et al.*, Applied Surface Science 257 (2011) 2717–2730
- [5] S. Jia *et al.*, J. Mater. Chem. A, 2022, 10, 251–265

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