Journal of Power Sources 279 (2015) 246–251

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A generalized method for high throughput in-situ experiment data analysis: An example of battery materials exploration

Bachir Aoun [a, *], Cun Yu [a], Longlong Fan [a], Zonghai Chen [b], Khalil Amine [b], Yang Ren [a]

[a] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
[b] Chemical Science and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

HIGHLIGHTS

- We report pre-modeling analysis methods to any ranked data set such as *in situ* XRD.
- We performed in-situ XRD and Rietveld refinement on Nickel rich cathode materials.
- Pearson's correlation unravels all major and minor changes through in-situ XRD data.
- Scedasticity formalism explores the reactivity and formation pathway during synthesis.

ARTICLE INFO

Article history:
Received 3 November 2014
Received in revised form
17 December 2014
Accepted 5 January 2015
Available online 6 January 2015

Keywords:
Lithium ion batteries
Cathode materials
Batteries materials
In-situ analysis method

ABSTRACT

A generalized method is introduced to extract critical information from series of ranked correlated data. The method is generally applicable to all types of spectra evolving as a function of any arbitrary parameter. This approach is based on correlation functions and statistical scedasticity formalism. Numerous challenges in analyzing high throughput experimental data can be tackled using the herein proposed method. We applied this method to understand the reactivity pathway and formation mechanism of a Li-ion battery cathode material during high temperature synthesis using in-situ high-energy X-ray diffraction. We demonstrate that Pearson's correlation function can easily unravel all major phase transition and, more importantly, the minor structural changes which cannot be revealed by conventionally inspecting the series of diffraction patterns. Furthermore, a two-dimensional (2D) reactivity pattern calculated as the scedasticity along all measured reciprocal space of all successive diffraction pattern pairs unveils clearly the structural evolution path and the active areas of interest during the synthesis. The methods described here can be readily used for on-the-fly data analysis during various in-situ operando experiments in order to quickly evaluate and optimize experimental conditions, as well as for post data analysis and large data mining where considerable amount of data hinders the feasibility of the investigation through point-by-point inspection.

Published by Elsevier B.V.

1. Introduction

The development of faster sensors, detectors and instruments has been continuously accelerating data acquisition speed and enlarging data volume in the field of both basic and applied research. The availability of state-of-the-art high throughput tools and techniques, especially at large user facilities like Advanced Photon Source (APS), has significantly facilitated the in-situ operando exploration of advanced materials in real time and realistic conditions. However, due to the rapid data collection and large data volume, the conventional approach to analyze and inspect each spectrum becomes inefficient and sometimes unfeasible. It is particularly important for researchers to quickly evaluate results during the experiment, in order to decide if there is any critical parameter or region for improved experimental conditions and better results. There is an urgent and increasing demand for a fast and universal method to interrogate high throughput experimental data sets for both on-the-fly and post data analysis. Such a method will help uncover data insights to accelerate scientific discovery and innovation. In this paper, we report a generalized method based on correlation functions and statistical scedasticity formalism to extract important information of series of spectra as a

* Corresponding author.
E-mail address: baoun@aps.anl.gov (B. Aoun).

http://dx.doi.org/10.1016/j.jpowsour.2015.01.033
0378-7753/Published by Elsevier B.V.

function of any type of variable. We demonstrate its capability by applying this method to explore the reactivity pathway and formation mechanism during high temperature synthesis, which are widely used for making cathode materials for Li-ion batteries.

Lithium transition metal oxides are dominant cathode materials for lithium-ion batteries that power the modern portable electronics. Substantial amount of effort has been devoted to formulating an optimal chemical composition and a proper process to maximize the electrochemical performance and life of such cathode materials [1–7]. Most of the incremental improvement reported in the open literature is mostly accomplished by try-and-error approach [4–7] due to the lack of a systematic and fundamental study of material behavior during the preparation of such materials. This has been a common dilemma in the general field of the material science. The high-intensity, high-quality X-ray source generated at cutting-edge synchrotron facilities has enabled us to investigate the real materials in real devices at a realistic condition. The latest development of temporal/special resolved techniques provide us unprecedented multidimensional characterization power to establish the structure-property relationship of functional materials [8–10]. However, the full utilization of such instrumental power is barely achieved because the prior knowledge/experience is generally sought after for manual data reduction before a feasible in-depth analysis can be carried out. This sometime leads to a systematic "ignorance" of some subtle information that is of great scientific value.

Recently, *in situ* synchrotron probes are extensively utilized to investigate batteries materials during the synthesis [11–13], during the normal operation of batteries [14,15], as well as during the abuse of battery materials [15–17]. The latest development of synchrotron technologies enable us to collect thousands of spectra for a single experiment, and the exhaustive processing of the experimental data becomes less and less possible. Very often, one needs to identify the most important region of interest for detailed data analysis [15,17]. Alternatively, computer-based mathematical tools are often pursued for the data reduction and data process to minimize the unnecessary influence of prior knowledge. For instance, Cui et al. carried out *in situ* X-ray Absorption Near Edge Spectroscopy (XANES) to study the (de)lithiation mechanism of SeS_x anode material for lithium-ion batteries. Using the residual error of linear combination analysis as an indicator, Cui et al. was able to identify the existence and the chemical composition of intermediate compounds (Li_2Se_2 and Li_2Se_4) during the charge/discharge of SeS_x anode [18]. Similarly, Piao et al. used factor analysis (FA) to process the *in situ* XANES data during the charge/discharge of $LiVPO_4F$ cathode, and was able to predict the existence of an intermediate phase Li_xVPO_4F during the charge/discharge process [19]. Kan et al. used evolutionary factor analysis (EFA) to analyze the *in situ* XANES data during the solid state synthesis of Li_2MnO_3 using $MnCO_3$ and Li_2CO_3 as the starting materials. Without the need of prior knowledge, the EFA was able to extract the evolution profile and the pure XANES spectrum of an intermediate compound, determined to be MnO_2, which was not able to be characterized by *in situ* high energy X-ray diffraction (HEXRD) [20]. In this work, we utilize *in situ* HEXRD to track the structural evolution during the solid state synthesis of $LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2$, a promising high energy-density cathode material for lithium-ion batteries. Due to the complexity and non-linear nature of XRD data, above linear-algebra-based algorithms are not suitable for processing *in situ* HEXRD data. Therefore, Pearson's correlation functions and statistical scedasticity formalism are proposed herein to mathematically detect the subtle change of HEXRD patterns during the *in situ* experiment.

2. Experimental details

The powders of $(Mn_{0.15}Ni_{0.7}Co_{0.15})CO_3$ and Li_2MnO_3 were mixed with a molar ratio of 2:1, and cool-pressed into a pellet, about 2 mm in thickness and 7 mm in diameter. The precursor $(Mn_{0.15}Ni_{0.7}Co_{0.15})CO_3$ was prepared using a co-precipitation method reported in our previous papers [1,2]. The pellet was then placed in a Linkam high temperature furnace TS1500. The in-situ high-energy X-ray diffraction experiment with a transmission mode was performed at the beam line 11-ID-C of the Advanced Photon Source (APS), at Argonne National Laboratory. The wavelength of the X-rays was 0.11165 Å. Two-dimensional (2D) HEXRD patterns were collected continuously using a Perkin–Elmer large area detector when the sample was heated up from room temperature up to 850 °C with a constant heating rate of 1 °C per minute. The 2D patterns were calibrated and converted to the conventional patterns of intensity versus 2-theta using Fit2d software. The temperature dependent HEXRD patterns are shown as a contour plot in Fig. 1. Details of the experimental setup and data treatment can be found in our previous report [17].

3. Correlation analysis

Correlation methods are commonly used to extract signal from background noise and to measure dependence between two sets of data. Noda has discussed the procedure of generating 2D correlation spectra from infrared spectroscopy [21–23] and he has shown that a two-dimensional covariance map can be calculated for any ranked spectral data sets (equation 18 in ref 23) [23]. Faguy and Balachander [24] showed that by analyzing infrared spectroscopy data using Noda's two. dimensional covariance analyses, it becomes possible to determine methyl and methylene stretching modes of lithium perchlorate diethyl ether electrolyte solutions where it was previously thought to show no solute solvent dependent bands in the mid-Infrared spectra. Here our aim is to unravel the fine details and to easily identify the interesting temperature dependent in-situ X-rays diffraction data ranges that need more attention and studying. Firstly, we calculated Noda's normalized covariance matrix '*CM*' (equation (1.1)).

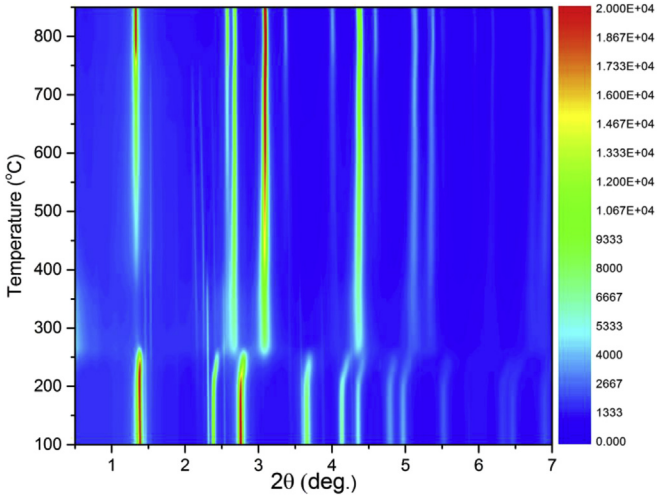

Fig. 1. Temperature dependent HEXRD patterns during the solid state synthesis of $Li(Ni_{0.7}Mn_{0.15}Co_{0.15})O_2$ using $(Ni_{0.7}Mn_{0.15}Co_{0.15})CO_3$ and Li_2CO_3 as starting materials.