Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

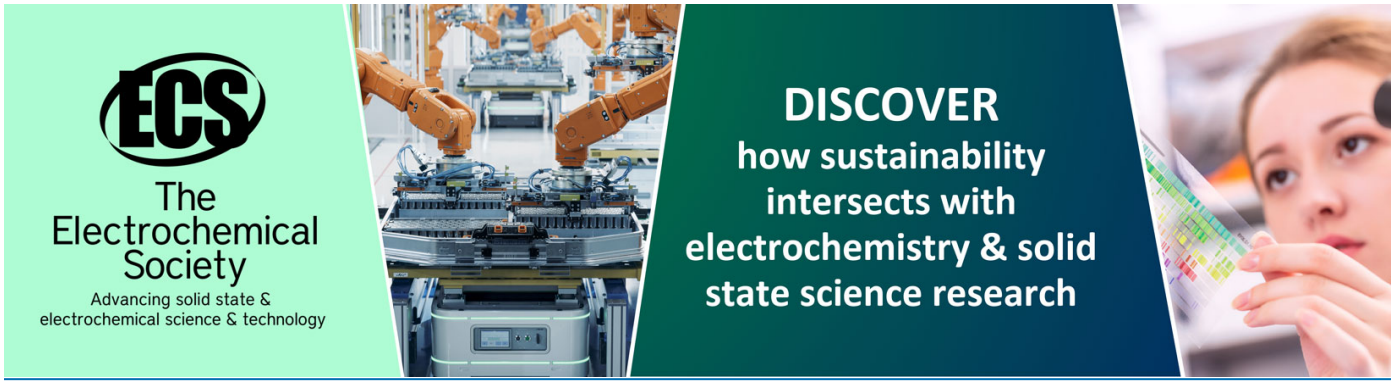
In-situ battery measurement of $LiFePO_4$ cathode during charge mechanism using x-ray diffraction

To cite this article: Evangelin Hutamaningtyas *et al* 2020 *J. Phys.: Conf. Ser.* **1436** 012082

View the article online for updates and enhancements.

You may also like

- Temperature Effect on LiFePO4 Cathode Performance
Abdelbast Guerfi, Nathalie Ravet, Patrick Charest et al.
- Modeling of LiFePO4 battery open circuit voltage hysteresis based on recursive discrete Preisach model
Wei-Yi Sun, , Hai-Tao Min et al.
- Thermodynamically Consistent and Computationally Efficient 0D Lithium Intercalation Model of a Phase Separating Cathode Particle
Klemen Zeli and Tomaž Katrašnik



This content was downloaded from IP address 3.145.47.253 on 05/05/2024 at 16:56

In-situ battery measurement of $LiFePO_4$ cathode during charge mechanism using x-ray diffraction

Evangelin Hutamaningtyas, Sudaryanto, Bambang Sugeng, Wagiyo Honggowiranto and Evvy Kartini

Center for Science & Technology of Advanced Material – National Nuclear Energy Agency of Indonesia BATAN Puspiptek Gd.71, Tangerang Selatan, Banten 15314, Indonesia

e-mail: evangelinh@batan.go.id

Abstract. Lithium-ion batteries (LIB) as one of the essential rechargeable energy storage for supporting renewable technologies is currently a big issue. It is important to understand the mechanism of lithium-ion batteries in order to improve more durable batteries, long cyclable ability and better efficiency. This work aimed to use in-situ X-ray diffraction (XRD) as a powerful technique for acquiring a fundamental understanding of structure and phase transformations of lithium-ion battery during charge mechanism. The battery consists of $LiFePO_4$ as cathode and graphite as anode material. The results show that some new Bragg peaks occur at 2θ of 39.97° and 47.26°. These indicate a phase transformation occurred from $LiFePO_4$ to $FePO_4$ during the charging mechanism. It can be concluded that in-situ XRD is a powerful tool to understand the phase transformation of lithium-ion batteries during the charging mechanism.

1. Introduction

Lithium-ion batteries (LIB) is one of the essential rechargeable energy storage for supporting the renewable technologies. This related to their high energy density so it can be used as the automotive industry, for powering a hybrid and pure electric vehicle. The high demand for LIB has stimulated the research and development of its advanced materials, different battery models and some measurement tools so that it could lead to better performance and understanding the natural process of it[1,2].

Research efforts have been made to develop the desirable characteristics of LIB such as large storage capacity, fast kinetic ions movement and long term cyclability. Among these research inspired by Goodenough et al's[3], the olivine phase lithium iron phosphate ($LiFePO_4$) has been studied extensively as a promising cathode material. $LiFePO_4$ has a high specific capacity, excellent thermal stability, and stable cyclability. It proved to be one of the most attractive and considered cathodes for hybrid and pure electric vehicle batteries. Nevertheless, the understanding of the mechanism during charge and discharge has not been known[1].

The real-time method for understanding lithium storage properties could be an answer to guide the development of more durable batteries, long cyclable ability and better efficiency. Direct measurement of lithium during charge-discharge processes within a material in real-time can provide insightful information for modeling lithium-ion transport at the fundamental part and full systems level. During charge and discharge processes, many methods such as Mossbauer spectroscopy, transmission electron microscopy[4,5], scanning probe microscopy (AFM, STM)[6,7], and X-ray techniques have been done

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

to study the changing phenomena. Some reports on X-ray studies on LIB such as X-ray absorption spectroscopy (XAS), transmission X-ray microscope, X-ray radiography, and X-ray diffraction. XAS is being preferred for obtaining detailed information on electronic structure and order[8]. Otherwise, a transmission X-ray microscope is used for studying structural and phase compositions[9]. Meanwhile, X-ray radiography is used to investigate and visualize the lithiation process as well as the significant volume expansion of electrode materials[10]. As for X-ray diffraction the focus was to study the self-growing of batteries[2,11]. Each method is having their own qualifications and limitations[12-15].

Some research related to the development of LIB has been done extensively in the various institution in Indonesia. The integrated battery laboratory of BATAN focuses on developing electrode materials[16,17]. However, the detailed study of the standard procedure on in-situ battery during charge in Indonesia has not been studied yet. This work aimed to observe the structure mechanism lithium-ion battery during charge by XRD. The electrochemical cell consisted of $LiFePO_4$ as cathode and graphite as anode material.

2. Experimental details

2.1. Materials

The cathode materials were purchased from MTI Cor. The USA such as $LiFePO_4$ black powder with grain size D90 of 15 μm, 1.45 g/cm^3 tapped density, and 1.3% carbon content, polyvinylidene difluoride (PVDF) white powder with 99.5% purity and molecular weight of 600,000 as the binder. Conductive graphite with 99.98 fixed carbon and 1-5 μm granularity was used as the anode. The electrolyte was commercial available 1.0 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1, v/v) as the electrolyte and celgard 2400 polyethylene was used as the separator. Aluminum and copper foils were purchased from MTI Cor. USA.

2.2. Preparing the battery cell and battery assembly

The composites electrodes for in situ XRD cells were made of slurries with some stoichiometric solutions of $LiFePO_4$: carbon black: binder in NMP. Those steps also were done for graphite as anode materials. Both of cathode and anode materials were prepared as a slurry in some stoichiometric solution and the depositions followed by an aluminum foil as the current collector for the cathode, while copper foil as the current collector for the anode. The sample preparation and characterization were performed at the Integrated Battery Laboratory, PSTBM, BATAN, Indonesia.

As schematically illustrated in Figure 1, the in situ XRD cell consists of a top cover, a retainer, a beryllium window, two Viton O-sealing rings (upper and lower diameters are 1 inch and 22 mm with thickness of 2 mm for both), cathode, separator and anode as described above, and lower housing named Teflon. At the bottom of the lower housing part, there are two holes shown by red wires to connect it with charge-discharge tools at XRD. The in situ XRD cell was made by a PANalytical company.

The most important thing in preparing the in situ XRD cell was cleaning thoroughly. Every part of the cell must be cleaned so there is no excessive dirt that can disturb the contact of electrode materials. Dimethyl carbonate (DMC) and acetone were used as a chemical cleaner. For the beryllium window the cleaning steps were done using the ultrasonic cleaner at 50°C for 30 minutes. After making sure that every part was clean, the resistances of every part were checked using a multimeter and it should be less than 1 Ohm. When the in situ XRD cell and the electrode materials were ready, the assembly of the cell was being done at the glove box with the addition of $LiPF_6$ as electrolyte with a configuration like shown in Figure 1. The cell was ready to be studied with in situ XRD battery measurement.

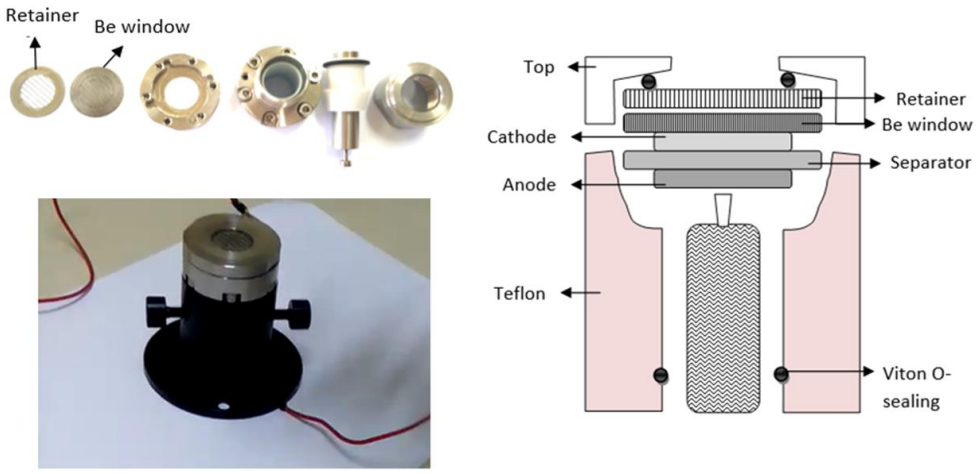


Figure 1. Schematics of in situ electrochemical cell for XRD technique

2.3. In-Situ XRD setup

The picture of the setup is displayed in Figure 2. For in situ XRD study, XRD of PANalytical instrument using copper at λ Kα1 1.54Å with voltage and current set to 40 kV and 10 mA, respectively, was used. The open aperture of ½ was used for in situ XRD battery measurement. The cell was placed at a multi-purpose sample stage. The measurement of phase transitions was continuously recorded by a static line detector (1D). The XRD measurement was conducted during the battery charging process from open circuit voltage 1.5V up to 3.8V using 1.5 mA of the constant current following by constant voltage at 3.8V. The X-ray diffraction patterns were compared with the database of ICSD. All the sample preparation and in situ XRD battery measurements were performed at the Integrated Battery Laboratory, Center for Science and Technology of Advanced Materials (PSTBM), BATAN, Indonesia.

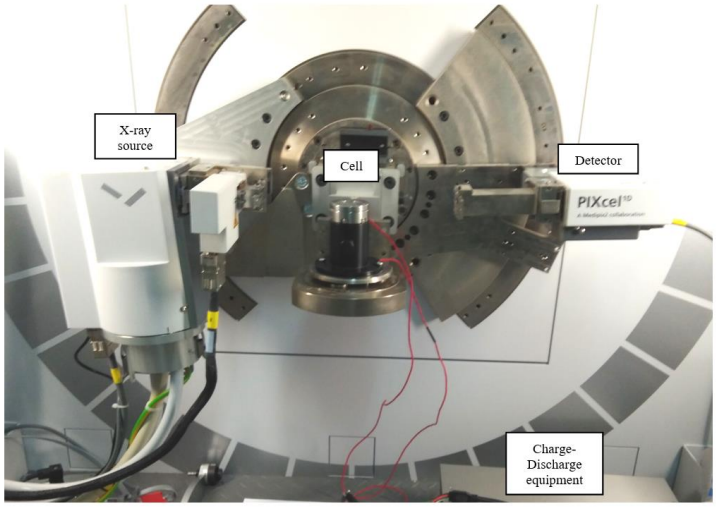


Figure. 2 The setup of in situ XRD battery measurement

3. Result and Discussion

The initial $LiFePO_4$ at first in-situ XRD measurement is shown in Figure 3. Some sharp intense peaks are observed in these two cases at 45.83°, 50.96° and 52.83°. Those peaks proved by the ICSD reference no. 96-901-2033 as beryllium with three peaks as the contribution peaks of Be window at electrochemical XRD cell battery. The XRD patterns indicate well-resolved diffraction peaks, that indexed to orthorhombic lattice structure in the *Pnma* space group LFP similar to previous work[16]. During charge mechanism, the extraction of lithium from LFP may be described as[3]:

$$LiFePO_4 - xLi^+ - xe^- \rightarrow xFePO_4 + (1-x)LiFePO_4 \quad [1]$$

By that equation, lithium ions are extracted from LFP and the second phase of $FePO_4$ is formed with some of LFP still in the process of extraction. According to Zhang et al. (2011), phase transformation in LFP during charge and discharge mechanism appears to depend on the synthesis method, particle size, surface coating, charging rate and testing procedures[1]. This means that the charging rate and testing procedures have a distinct impact on the result of the Li-ion movement rate and the phase transformation of it.

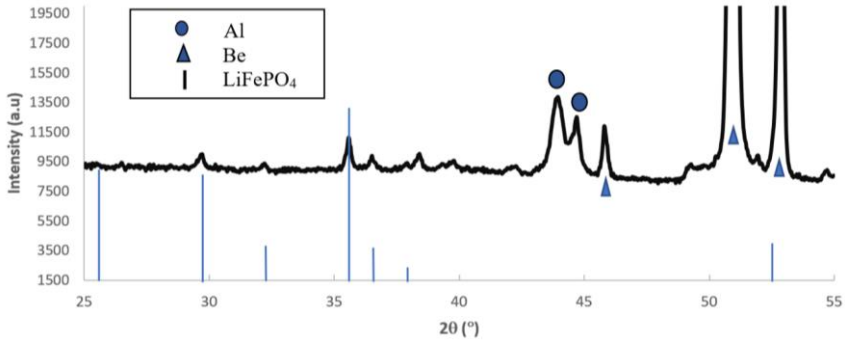


Figure 3. XRD pattern of initial $LiFePO_4$ at first in-situ XRD measurement

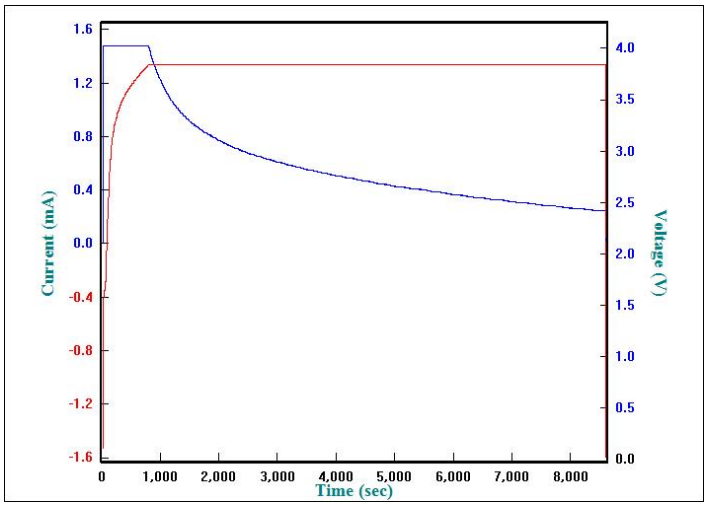


Figure 4. Time dependence on current and voltage during charge mechanism of $LiFePO_4$

Figure 4 showed the time dependence of current and voltage during the charging mechanism of $LiFePO_4$. Results from XRD patterns and charge data had correlation at a time scan. The charging mechanism was conducted in constant current continued by constant voltage process. At first, around 1000 seconds of time experiment, the battery was charged in the constant current mode of 1.464 mA and continued in constant voltage of 3.8 V. The charge process was conducted for 8500 seconds. As we can see, until 8500 seconds, the charging mechanism was still in constant voltage mode. This indicates that the battery was not near the full charge yet, and need more time to achieve the full charge. Each of the XRD patterns from Figure5 equal to 7.5 minutes (450 seconds) of time dependence to current and voltage in Figure 4.

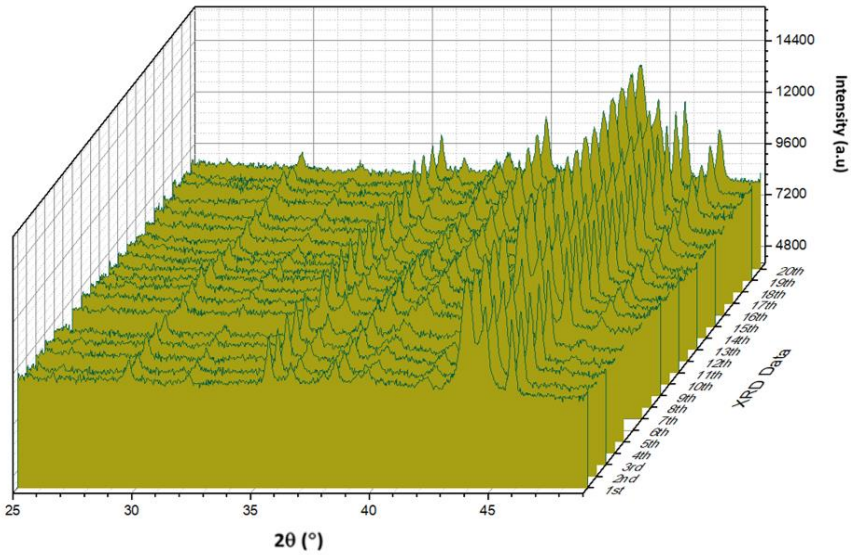


Figure 5. The three-dimensional (3D) image of in situ XRD battery measurement

The three-dimensional XRD data were shown in Figure 5. The diffractions data start from 2θ at 25° to 50°. These results achieved by conducting the in-situ experiment in the battery charge mechanism. The XRD patterns of $LiFePO_4$ battery matched with the ICSD reference pattern of lithium iron phosphate: 98-015-9107. From Figure 5, there is two distinct increments of intensities as seen at two peaks, 2θ of 39.97° and 47.26°. This result indicates some phase transitions during the charging mechanism of battery are observed. As a contrast, some other peaks showed no difference changes starting from the 1st data till 15th data.

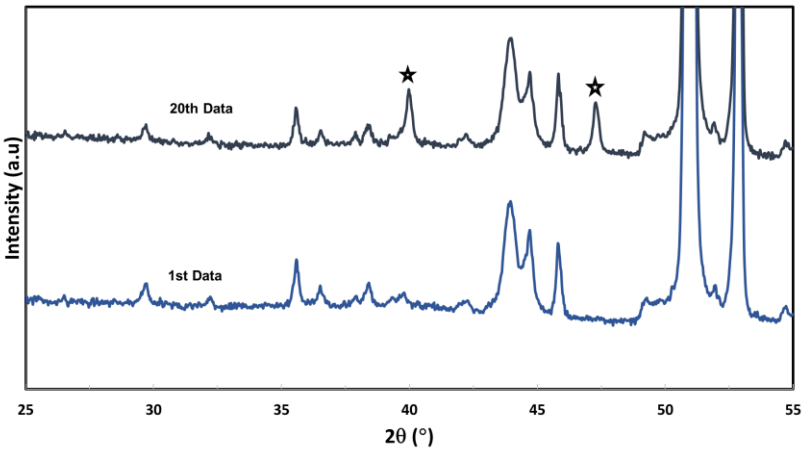


Figure 6. XRD patterns of $LiFePO_4$ battery during charge mechanism at 1st data and 15th data; reference patterns of $LiFePO_4$ and $FePO_4$. Note: the stars indicate the phase of $FePO_4$

In order to observe the phase transformation of the LFP cathode, the comparison data of the 1st and 20th XRD pattern was shown in Figure 6. Those two patterns are corresponding to the crystal structure of $LiFePO_4$ and $FePO_4$ phases from ICSD reference no. 98-015-9107 and 98-000-4266. It is clearly shown at 2θ of 39.97° and 47.26° from Fig 6 (star symbol) are the contribution of two-phase coexistence of $LiFePO_4$ and $FePO_4$ phases. However, the increasing intensities of those two distinct peaks are most likely know from the existence of the new $FePO_4$ phase during the charging process. On the other hand, the crystalline peaks of the $LiFePO_4$ phase remain stable in this diffraction angles.

This may due to the charging process still in halfway to reach the full charge. Another possible reason that the range of 2θ are too wide so the small angles are not covered, which in other work, the $LiFePO_4$ phase usually observed at small angles around 2°-18°, as shown by Takashi et. al.[14].

4. Conclusion

In situ study of $LiFePO_4$ cathode using X-ray battery measurement was conducted to investigate the phase transformation of $LiFePO_4$ during charge mechanism in full cell coupled with graphite as the anode. The assembled cell using a beryllium window was used. By means of in situ XRD pattern result during the charging mechanism of battery, some phase transformations from $LiFePO_4$ to $FePO_4$ were shown distinctly at 2θ of 39.97° and 47.26°. It can be concluded that in-situ XRD is a powerful tool to understand the phase transformation of lithium-ion batteries during the charging mechanism. This report also could show the standard procedure for other in situ studies of different materials LIB.

Acknowledgment

This study was carried out under the Center for Science and Technology of Advanced Materials – BATAN Budget Implementation List (DIPA) 2019 number 3446.001.001.

References

[1] Zhang W J 2011 *J. Power Sources* **196** 2962–70
[2] Zhu W, Liu D, Paolella A, Gagnon C, Ganepy V, Vijh A, and Zaghib K 2018 *Front. Energy Res.* **6** 1–16
[3] Padhi A K, Nanjundaswamy K S, and Goodenough J B 1997 *J. Electrochem. Soc.* **144** 1188
[4] Liu X H and Huang J Y 2011 *Energy Environ. Sci.* **4** 3844–60
[5] Liu X H, Liu Y, Kushima A, Zhang S, Zhu T, Li J, and Huang J Y *2012 Adv. Energy Mater.* **2** 722–41
[6] Orsini F, Du-Pasquier A, Beaudoin Bm Tarascon J M, Trentin M, Langenhuizen N, De Beer E, and Notten P 1998 *J. Power Source* **76** 19–29
[7] Raimann P R, Hochgatterer N S, Korepp C, Moller K C, Winter H, Schrottner H, Hofer F, Besenhard J O 2006 *Ionics* **12** 253–55
[8] Deb A, Bergmann U, Cramer S P, and Cairns E J 2007 *J. Electrochem. Soc.* **154** A534
[9] Chao S C, Yen Y C, Song Y F, Sheu H S, Wu H C, and Wu N L 2011 *J. Electrochem. Soc.* **158** A1335-39
[10] Sun F, Markotter H, Manke I, Hilger A, Alrwashdeh S S, Kardjilov N, Bnhart J 2017 *Appl. Surf. Sci.* **399** 359–66
[11] Liu D *et al* 2019 *Adv. Mater.***1806620** 1–57
[12] Siddique N A, Salehi A, Wei Z, Liu D, Sajjad S D, and Liu F 2015 *Chem. Phys. Chem.* **16** 2383–88
[13] Liu Q, Liu Y, Yang F, He H, Xiao X, Ren Y, Lu W, Stach E, and Xie J 2018 *ACS Appl. Mater. Interfaces* **10** 4622–29
[14] Takahashi I *et al* 2016 *J. Power Sources* **309** 122–26
[15] Liu D X, Wang J, Pan K, Qiu J, Canova M, Cao L R, Co A C 2014 *Angew. Chemie - Int. Ed.* **53** 9498–502
[16] Honggowiranto W and Kartini E 2016 *AIP Conf. Proc.*(American Institute of Physics LLC) **1710** 030045
[17] Ayu N I P, Kartini E, Prayogi L D, Faisal M, Supardi 2016 *Ionics* **22** 1051–57