

The improving conductivity of LiFePO₄ by optimizing the calendaring process

Deswita¹, Sudaryanto¹, H Djodi¹ and E Kartini¹

¹Centre for Science and Technology Advanced Materials, National Nuclear Energy Agency Build. 71 Puspiptek Area Serpong, Tangerang – Indonesia 15313

deswita@batan.go.id

Abstract. Lithium ion batteries have important applications in various electronic devices. The use of battery components such as LiFePO₄ cathodes determines battery performance. However, the electronic conductivity of LiFePO₄ is low; therefore, increasing the conductivity of the LiFePO₄ cathode sheet is very important. The aim of this research is to obtain the conductivity of LiFePO₄ cathode sheet which can be applied as lithium ion battery cathode through calendaring process optimization. LiFePO₄ cathode sheet preparation begins with LiFePO₄ slurry (LiFePO₄ + Carbon Black and PVDF / NMP) slurry, followed by coating it on Al foil surface, resulting in a sample denoted as C0. The calendaring process was then carried out to the cathode sheet, at 100°C by repeating once, twice, and three times, producing samples hereinafter referred to as C1, C2, and C3 respectively. LiFePO₄ cathode sheet products are characterized with X-ray diffractometer (XRD) and scanning electron microscopy (SEM) combined with energy-dispersive spectrophotometer (EDS) and LCR-meter. The XRD pattern shows that the LiFePO₄ cathode sheet consists of LiFePO₄ and carbon crystal phases. The cross-sectional microstructure of the LiFePO₄ cathode sheet shows that the sheets becomes denser and thinner as the number of calendaring increases. The thickness of the LiFePO₄ cathode sheet decreases with increasing calendaring process. The LiFePO₄ cathode sheet for the C0 sample was about 160µm in thick, and decreased gradually to 140, 130 and 120µm for the C1, C2 and C3 samples, respectively. The conductivity of the sample was improved from 9.9×10^{-5} to 2.9×10^{-5} , 3.0×10^{-4} , and 5.5×10^{-4} S.cm⁻¹. The density also was improved from 2.359 to 2.516 and to 2.638 g.cm⁻¹ with increasing calendaring process. It can be concluded that the optimizing calendaring process of the LiFePO₄ cathode sheet with the LiFePO₄ cathode sheet is important to improve the performance of batteries.

1. Introduction

Currently, the development of technology is running rapidly along with the growth and development of electronic equipment, especially cell phones and laptops. This electronic equipment requires the battery as its power source because it is used portably. To meet the growing need for portable power in the future, batteries are needed to provide large amounts of energy and power, and they need to be light, cheap, safe, and environmentally friendly [1–5]. In 1991 Sony first commercially produced lithium-ion battery; the production of lithium-ion batteries has increased significantly because it has created an electronic revolution in the world. Currently, Japan is the largest battery manufacturer, chiefly by Sony,



Panasonic, and Toshiba. Lithium-ion batteries are also the leader of battery products that control 46% or about 4 billion US dollars market share in 2007 [5, 6]. The lithium ion battery itself consists of anode, separator, electrolyte, and cathode. The cathode material is the most expensive material and one of the hardest to produce components of lithium ion batteries, and therefore intensive research is needed to focus on the cathode. The first cathode material used in lithium ion batteries is LiCoO_2 . Then other cathode materials such as LiMO_2 oxide compounds (M are metals which can be Co, Ni, Mn,), LiM_2O_4 spinel compound (M = Mn), and olivine LiMPO_4 (M = Fe, Mn, Ni, Co). LiFePO_4 is extensively developed as a cathode material because it is stable, cheap, and environmentally friendly. Efforts to improve electrical conductivity can be done in several ways, adding doping when synthesizing cathode material, and mixing cathode materials with metal powders or coating cathode materials with conductive carbon [7, 8]. In previous research, the standardization of LiFePO_4 cathode standard materials by adding carbon black has been performed [9–11], but has not yet obtained optimal conductivity. In this research, we produced LiFePO_4 cathode sheet by adding carbon black (CB) and polyvinylidene fluoride (PVDF) polymer in N-methylpyrrolidone (NMP) solution and variation of calendaring process [12–14]. Thus far, no other previous work has concerned the influence of the calendaring process. Therefore, in this study it is expected that through this calendaring process can produce the optimum LiFePO_4 material conductivity to be used as battery cathode material. The quality of the resulting product is characterized using the XRD to determine the phase of the LiFePO_4 . The density was calculated manually from measured mass and the volume of the sample. SEM-EDS to observe the surface morphology and its elements content. LCR meter to measure electrical conductivity.

2. Method

2.1 LiFePO_4 cathode sheet preparation

The materials used in this study include commercial materials such as polyvinylidene fluoride (PVDF) as binder, LiFePO_4 powder (LFP MTI), carbon black (CB) as additive, N-methylpyrrolidone (NMP) as solvent [5], and aluminum sheet (Al) as a current collector.

LiFePO_4 and CB powder of 85:10 (in weight percent ratio) [6] was mixed in agate mortar and then dried in oven at 80 °C for eight hours. The PVDF polymer of 5% by weight which only acts as a binder is dissolved in the MNP solvent and fed into mixer vacuum vial. Add the LiFePO_4 /CB mixture to the PVDF solution stirred with the vacuum mixer for 2 hours until a LiFePO_4 -shaped cathode of slurry is formed. LiFePO_4 cathode slurry is then superimposed (casting) on aluminum (Al) sheet foil using doctor blade, to form a LiFePO_4 cathode sheet. Then dried in a vacuum oven at 80 °C for 24 hours to obtain LiFePO_4 (one layer) cathode sheet. The slurry of the LiFePO_4 cathode sheet double layer is done in the same manner and composition. Furthermore, the slurry is coated on an uncoated Al foil sheet so that the aluminum sheet is centered between two LiFePO_4 slurries, then dried in a vacuum oven until a double layer LiFePO_4 cathode sheet is obtained. This sample is called a C0 sample that is ready for characterization. In a portion of the LiFePO_4 cathode sheet, a calendaring process was repeating for one, two and three times using a hot rolling machine [12] at a temperature about 100 °C, which are called C1, C2 and C3 samples. The detail cathode preparation has been described elsewhere [10].

2.2 LiFePO_4 cathode characterization

The phases inside the LiFePO_4 cathode sheet was measured using an X-ray diffractometer (XRD, PAN-analytical Empyrean), using a Cu-K irradiation source ($\lambda = 1.5406\text{\AA}$) in the range $2\theta = 10 - 80^\circ$, with a step size 0.5° and step time 10 seconds. The morphology and cross-sectional surface of the samples were observed with the Scanning Electron Microscope (SEM, JEOL - JSM 6510) equipment coupled with the energy-dispersive spectrophotometer (EDS) equipment. The conductivity of the LiFePO_4 cathode sheet was measured using impedance conductance resistance equipment (LCR meter, HIOKI LCR Hit ESTER 3532-50 for EIS). Silver paste as ion-blocking electrode and current collector was used on both sides of the samples. The impedance spectrum is measured in atmospheric environment and at room temperature using a voltage of 1 Volt and a frequency range of 100 Hz - 5MHz. The conductivity

of the sample was calculated from measured impedance value and the dimension of the sample. The density was calculated manually from measured mass and the volume of the sample.

3. Results and discussion

3.1 X-ray diffraction pattern (XRD)

The X-ray diffraction pattern has been measured using a $\text{CuK}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$), $2\theta = 10$ to 80° . Figure 1 shows the XRD pattern of LiFePO_4 cathode sheet samples before and after the calendaring process. The result shows that the sample has formed crystals well which is characterized by high and sharp diffraction patterns. The highest diffraction pattern lies at $2\theta = 35.8^\circ$ corresponding to the open data crystallography (COD). The material is lithium iron phosphate with LiFePO_4 chemical formula, Pnma space group (62), and orthorhombic crystal structure. The lattice parameter $a = 10.330 \text{ \AA}$, $b = 6.003 \text{ \AA}$, $c = 4.697 \text{ \AA}$ and atomic density (ρ) about $3.595 \text{ gram.cm}^{-3}$. The results are in agreement with the experiments performed by Wang Jiajun *et al.* (2015) [15] and Wang W. L *et al.* (2012) [9]. Yiu *et al.* [16] get results the lattice parameter from a LiFePO_4 without calendaring process of $a = 10.332 \text{ \AA}$, $b = 6.010 \text{ \AA}$, $c = 4.692 \text{ \AA}$. It is seen that there is no significant change in the crystals structure.

The diffraction pattern of the carbon phase is observed at $2\theta = 26.78^\circ$ as indicated by the sign (x) in Figure 1. Carbon or graphite with the formula C structured hexagonal crystals, group space P 63/mm (194), with parameters Lattice $a = b = 2.464 \text{ \AA}$, $c = 6.711 \text{ \AA}$ and density of $2.261 \text{ gram.cm}^{-3}$. The similarity of XRD patterns from all samples showed no change in crystal structure due to the calendaring process.

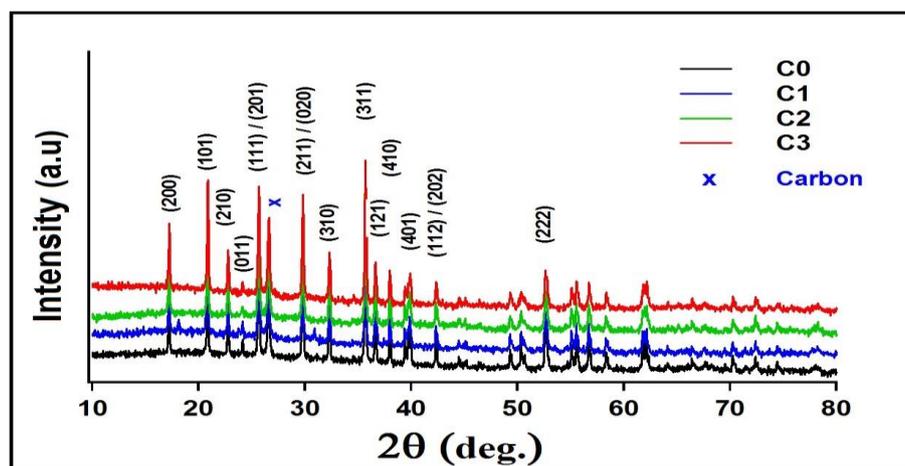


Figure 1. XRD pattern of LiFePO_4 cathode sheet for C0, C1, C2 and C3.

3.2 Scanning electron microscope (SEM)-energy disperse spectrophotometer (EDS)

Figure 2 is the microcrystalline sheet structure of LiFePO_4 cathode prior to calendaring (sample C0). The resulting particles ranged from 0.4 to $1.0 \mu\text{m}$, with the size measured on particles having clear grain boundaries. On the surface of the sample looking uneven and having many cavities, the polymer of PVDF appears to bind to the LiFePO_4 particles in the form of webs, as shown in Figure 2C0. Figure 2C1 is the microcrystalline sheet structure of LiFePO_4 after one round of the calendaring process (sample C1), the sample surface has not been uniform even though the calendaring process has been conducted and also still agglomerated. This is because after the calendaring process, the sample surface is covered by a PVDF polymer binder.

Figure 2(C2) is the microstructure of the calendaring C2 sample. Visible, the surface is more evenly distributed and the PVDF polymer integrates with the LiFePO_4 matrix and slightly cavities between one particle and the other evenly. The cavity in this cathode material is necessary to facilitate the movement of Li ions. Figure 2C3 is the microstructure of the sample after calendaring three times (C3). Can be

seen more evenly distributed sample surface with fewer cavities and solid, also seen some micro-cracks (micro cracks).

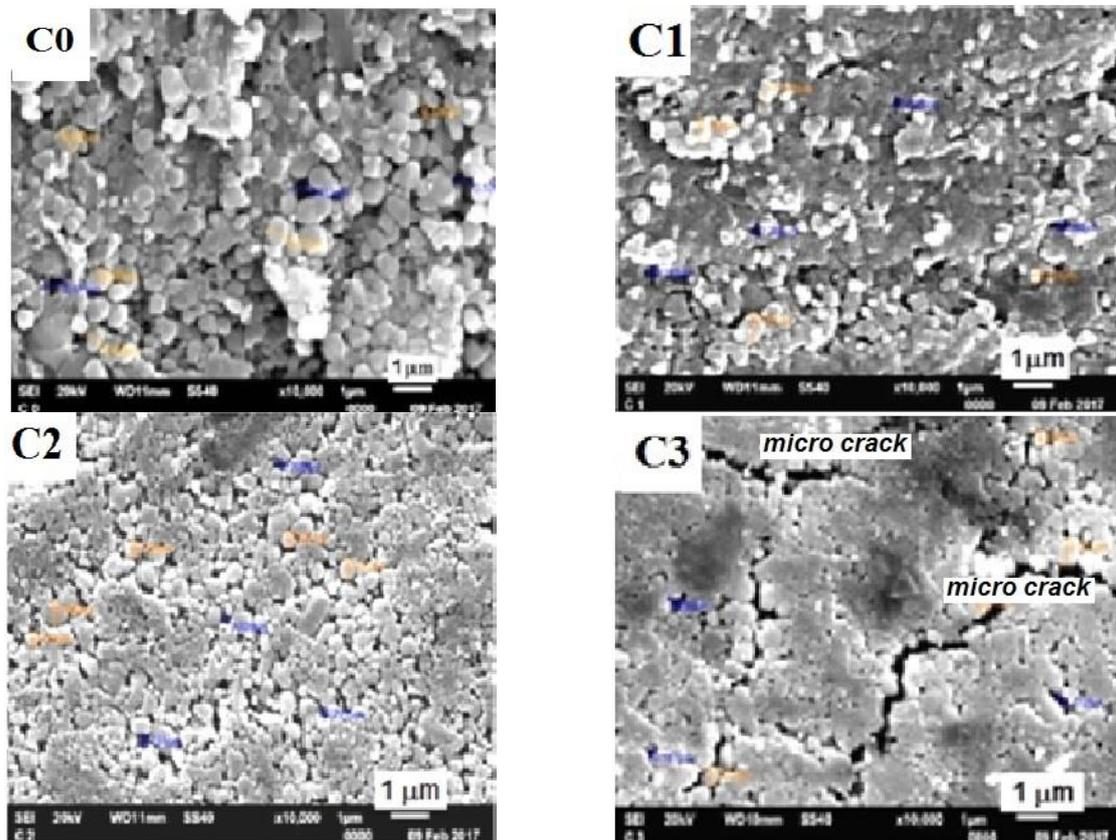


Figure 2. The microstructure of LiFePO_4 cathode sheet for C0, C1, C2 and C3.

Figure 3 shows the cross-sectional view of the LiFePO_4 cathode sheet before and after the calendaring process. The influence of calendaring process to the decrease of the LiFePO_4 cathode sheet thickness is described in Figure 4. Based on Figure 3 and Figure 4, LiFePO_4 cathode sheet thickness was obtained about $160\mu\text{m}$ (Figure 3C0). After several times calendaring process at a temperature of $100\text{ }^\circ\text{C}$, the thickness of the LiFePO_4 cathode sheet decreased to $140\mu\text{m}$ (12.50%), $130\mu\text{m}$ (18.75%), and $120\mu\text{m}$ (18.00%) respectively.

In the Figure 3(C0), the LiFePO_4 cathode material has not been perfectly attached to Aluminium (Al) foil as a current collector seen as a thin cavity above Al foil. In LiFePO_4 cathode material there is also a transverse cavity up to about $10\mu\text{m}$ in size. After the calendaring process for samples of C1, C2, and C3 LiFePO_4 cathodes with Al foil are well attached, they appear to be also denser with decreasing sample thickness, as shown in Figure 3C1 to Figure 3C3. The thickness vs. calendaring process is described in Figure 4.

In the calendaring C3 process, again appears the existence of micro-sized cracks, as shown in Figure 3C3. To determine the conductivity of the effect of the calendaring process, the sample was then measured with LCR meter equipment as shown in Figure 9.

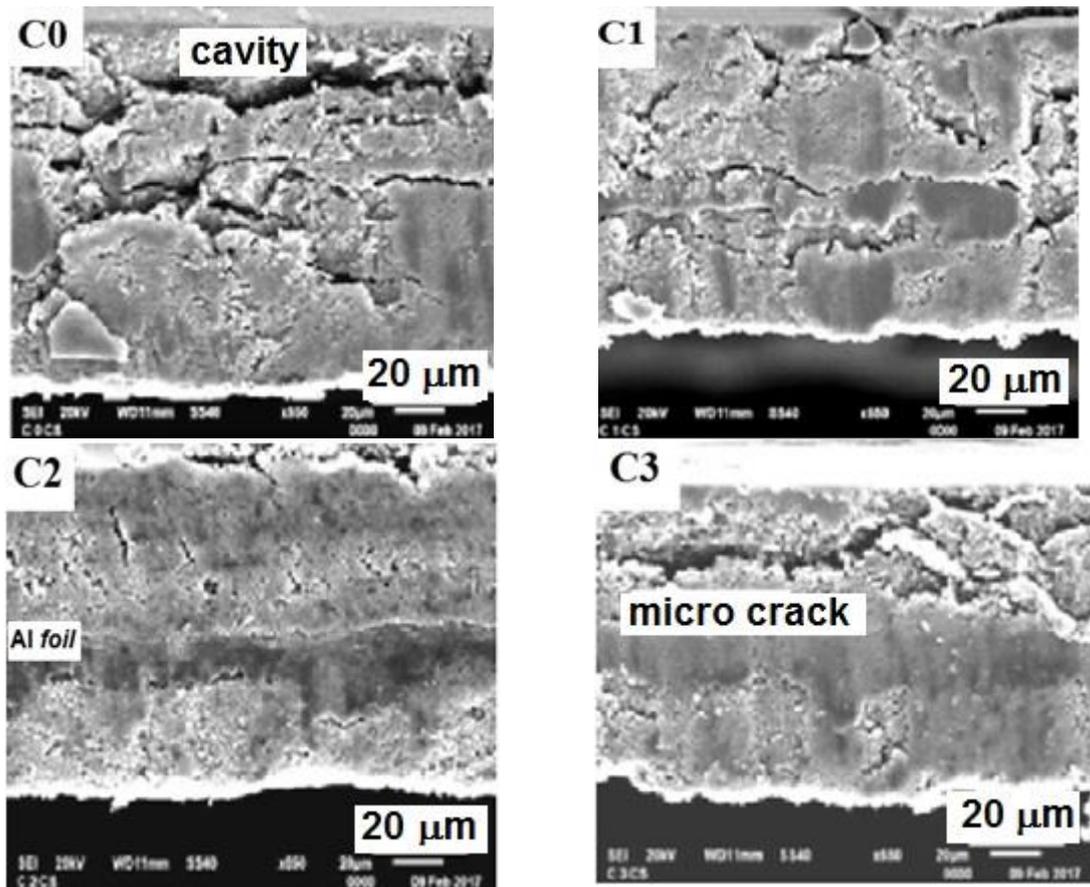


Figure 3. The cross section of LiFePO_4 cathode sheet for C0, C1, C2 and C3.

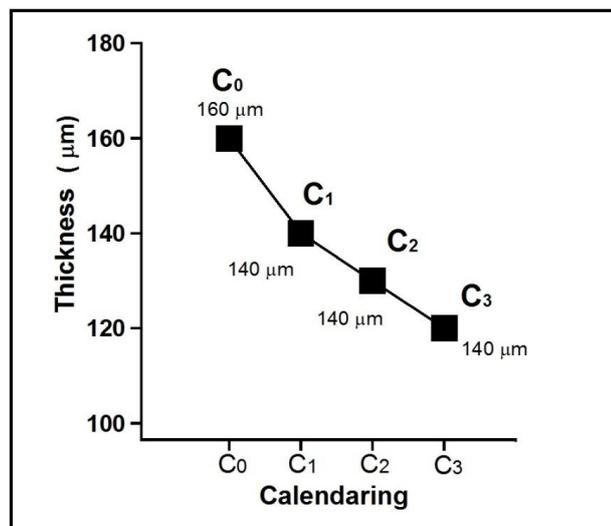


Figure 4. The influence of calendaring process to the thickness of LiFePO_4 cathode sheets.

The SEM-EDS is only capable for detecting elements with an atomic number of more than 5, so Li cannot be detected because its atomic number is 3 [16]. Figure 5 shows the percent mass curve of the

calendaring process. From Figure 5 it appears that the elements of Fe and P representing elements of LiFePO_4 increase with the increase of calendaring process. The F value representing the PVDF polymer seen in C1 is an increase in the percent mass of F. This shows that the PVDF polymer binder covers the LiFePO_4 surface, as shown in the microstructure of Figure 2 of C1 sample. With the increase in calendaring processes (samples C2 and C3) the F element decreases, which shows the LiFePO_4 surface not covered by the PVDF polymer binder seen in the microstructure Figure 2 samples C2 and C3.

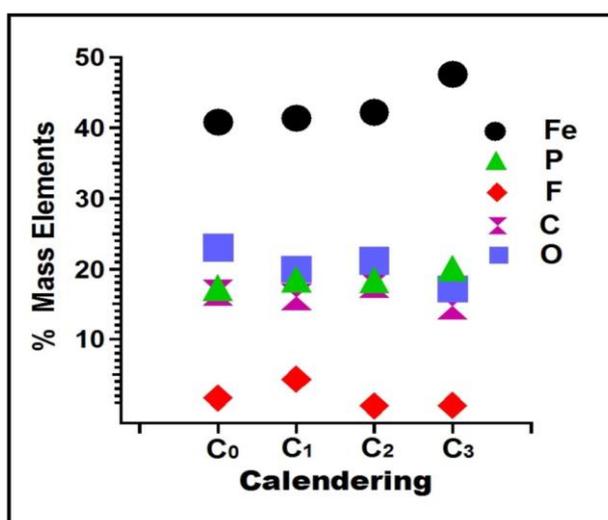


Figure 5. EDS counting result (in mass percent) of the element for C0, C1, C2 and C3.

3.3 Impedance conductance resistance (LCR meter)

The conductivity (σ) of the electrode is calculated from the measured impedance value on LCR meters and electrolytic dimensions such as the thickness and surface area of the sample. Figure 6 shows the conductivity change (σ) of the LiFePO_4 cathode sheet against the frequency measured at room temperature, while Figure 7 shows the influence of calendaring process to the change of the LiFePO_4 cathode sheet conductivity. From Figure 6 and Figure 7, the conductivity value of C0 is about $9.8 \times 10^{-5} \text{ S.cm}^{-1}$. The conductivity of the C sample is obtained as about $2.9 \times 10^{-5} \text{ S.cm}^{-1}$. The decrease in conduc-

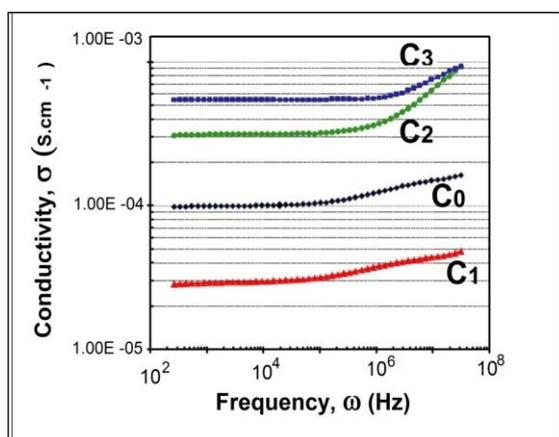


Figure 6. Conductivity curve vs. Frequency of LiFePO_4 cathode sheet for C0, C1, C2, and C3.

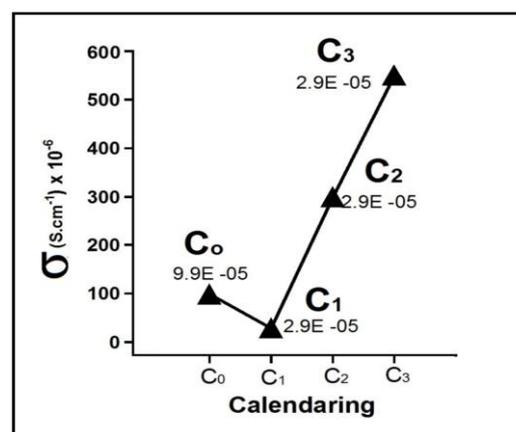


Figure 7. Conductivity curve vs. calendaring of LiFePO_4 cathode sheet for C0, C1, C2, and C3.

tivity of the C1 sample may be due to the closed surface of the sample by the PVDF polymer acting as a binder. In the calendaring process, the C2 conductivity sample increased significantly to $3.0 \times 10^{-4} \text{ S.cm}^{-1}$. The increase of significant conductivity values from sample C1 to C2 may be the shrinking of the PVDF polymer binder from the sample surface, thus increasing the electrical contact and increasing the concentration of mobile ions. Then the conductivity on the C3 sample increased to $5.5 \times 10^{-4} \text{ S.cm}^{-1}$ after calendaring 3 times. This increase is not very significant, because it is still one order with a sample of C2. Synthesis of LiFePO_4 cathode sheets by hydrothermal process has been carried out with the conductivity obtained being about $5.6 \times 10^{-5} \text{ S.cm}^{-1}$ [17].

3.4 Density

The density of the sample was calculated manually from measured mass and the volume of the sample. Figure 8 shows the density curve of the LiFePO_4 cathode sheet through calendaring process. It is seen that the density of cathode sheets of LiFePO_4 sample C1 increases the calendaring process until it reaches the highest value in calendaring process C2. This means that the density of the sample is getting denser and thinner with increasing calendaring process. The density of the LiFePO_4 cathode sheet then decreases with the continuation of the calendaring process up to C3, as described in Figure 8. The decrease in the C3 sample density is due to the formation of micro-size cracks formed during the calendaring process, as shown by SEM morphology in Figure 2 and Figure 3. This causes C3 samples to be impossible to apply as LiFePO_4 cathode sheets on lithium ion batteries.

From Figure 8, it is seen that through the calendaring process, the density of the LiFePO_4 cathode sheet is more denser. When the density of LiFePO_4 cathode sheet increases, then the conductivity also rises, as shown in Figure 7 and Figure 8. It is clear that the calendaring process can solidify the LiFePO_4 cathode sheets causing the microstructure to be better organized with a much smoother surface, thereby enhancing electrical contact and increasing concentration Mobile ions that occur through the Li^+ ion leap mechanism. In addition, the PVDF polymer used to make the electrolytic membrane has a high enough mechanical strength to withstand the pressure between the cathode and anode, has a high degree of chemical stability and ionic conductivity, easy to make in thin size, has thermal stability, has dimensional stability or size, and able to form a nice interface with electrodes. As a result, the conductivity of the LiFePO_4 cathode sheet results in increased calendaring process.

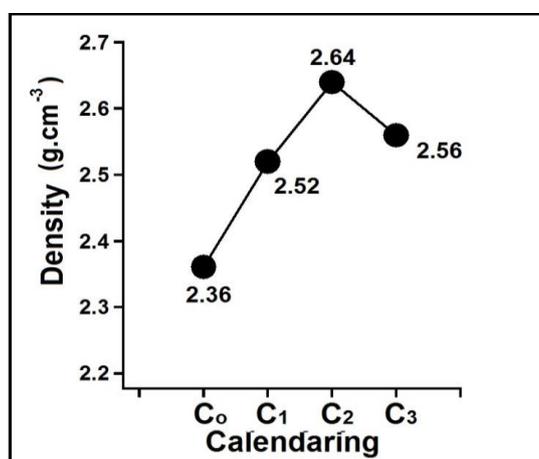


Figure 8. The density of LiFePO_4 cathode sheet vs. calendaring process for C0, C1, C2 and C3.

4. Conclusion

LiFePO_4 cathode sheets have been prepared from LiFePO_4 , carbon black (CB), and polyvinylidene fluoride (PVDF/NMP) powder mixtures. The improvement of the LiFePO_4 cathode sheet conductivity

has been successfully performed by calendaring process optimization. The XRD pattern shows that the LiFePO_4 cathode sheet consists of LiFePO_4 and carbon crystal phases. The cross-sectional microstructure of the LiFePO_4 cathode sheet shows the sheets getting denser and thinner as the number of calendaring increases. The thickness of the LiFePO_4 cathode sheet obtained by the calendaring process about $160\mu\text{m}$ then decreased about 12.5% to $140\mu\text{m}$, 18.75% to $130\mu\text{m}$, and 25.00% to $120\mu\text{m}$ with the increase of calendaring process. The conductivity of the LiFePO_4 cathode sheet obtained is 9.9×10^{-5} ; 2.9×10^{-5} , 3.0×10^{-4} , and 5.5×10^{-4} $\text{S}\cdot\text{cm}^{-1}$ for samples C0, C1, C2, and C3, respectively. It can be concluded that the calendaring process can increase the conductivity of the LiFePO_4 cathode sheet with the LiFePO_4 cathode sheet.

Acknowledgment

This study is a part of the the Battery Group research Programs in the Center for Advanced Materials Science and Technology, and funded by DIPA PSTBM-BATAN for Fiscal Year 2017.

References

- [1] Kartini E Honggowiranto W Jodi H and Jahya A K Adams S Kawamura J 2014 (*Eds*) *Proc. the 14th Asian Conf. Solid State Ionics* Singapore Research Publishing 163–73
- [2] Jodi H Zulfia A Deswita and Kartini E 2016 *Int. J. Technol.* **8** 1117–26
- [3] Johnson I D Blagovidova E Dingwall P A Brett D J Shearing P R and Darr J A 2016 *J. Power Sources*, **326** 476–81
- [4] Yurwendra A O and Noerochim L 2014 *J. POMITS Tech.* **3(2)** F229–31
- [5] Nur I P A Kartini E Dwi P L Faisal M and Supardi 2016 *Int. J. Ionics* **22(7)** 1051–7
- [6] Scipioni R Jurgensen P S Ngo D T Simonsen S B Liu Z Yakal-Kremski K J Wang H Hjelm J Norby P Barnett S A and Jensen S H 2016 *J. Power Sources* **307** 259–69
- [7] Halim A Widiastuti W Setyawan H Machmudah S Nurtono T and Winardi S 2014 *AIP Conf. Proc.* **173(1586)** 173–8
- [8] Triwibowo J Lestariningsih T Priyono S Purawiardi R I and Daulay L 2015 *J. Mater. Energy Indones.* **5(2)** 1–7
- [9] Li-Wang W Jin E M and Gu H B 2012 *Trans. Electr. Electron. Mater.* **13(3)** 121–4
- [10] W Honggowiranto and Gunawan I 2015 *Proc. Nat. Sem. XXIV Chem. in Indust. and Envi.* 57–64
- [11] Deswita and Gunawan I 2016 *Proc. Nat. Semin. XIX Chem. in Develop.* 69–74
- [12] Haselrieder W Ivanov S Christen D K Bockholt H and Kwade A 2013 *ECS Trans.* **50(26)** 59–70
- [13] Smekens J Gopalakrishnan R Van den Steen N Omar N Hegazy O Hubins A and Van Mierlo J 2016 *Energies* **104(9)** 2–12
- [14] Van-Bommel A and Divigalpitiya R 2012 *J. Electrochem. Soc.* **159(11)** A1791–5
- [15] Wang J and Sun X 2015 *Energy Environ. Sci.* **8** 1110–38
- [16] Yiu Y M Yang S Wang D Sun X and Sham T K 2013 *J. Phys. Conf. Ser.* **430(1)** 2014
- [17] Ding Z Gu K Zheng H Liu C Liu L Yan L X and Guo 2014 *Electrochim. Acta* **146** 585–59