CHARACTERIZATION AND ELECTROCHEMISTRY OF LiFePO$_4$ SYNTHESIZED BY SONICATION-HYDROTHERMAL METHODS

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ABSTRACT

CHARACTERIZATION AND ELECTROCHEMISTRY OF LiFePO$_4$ BY SONICATION-HYDROTHERMAL METHODS. Cathode materials of LiFePO$_4$ for rechargeable-lithium ion battery were synthesized by combination of sonication and hydrothermal method. The reaction has been carried out by mixing of FeSO$_4$.7H$_2$O, H$_3$PO$_4$, LiOH and ethylene glycol. The mixtures were sonicated by ultrasonic prior to a hydrothermal process. The crystal structure, microstructure and electrical properties of LiFePO$_4$ products were characterized by using X-ray diffraction (XRD), a Scanning Electron Microscope (SEM), and an Impedance Spectroscopy, respectively. The X-ray data showed that the crystal structure of LiFePO$_4$ belongs to the *P m n a* space group (olivine structure). The crystalline size of sample non-sonic, sonic and commercial LiFePO$_4$ were 730.2; 3068.0 and 639.4 Å, respectively. Performances of half cell batteries were measured by Impedance spectroscopy and by using Battery Analyzer BST-8.The EIS data from half cell batteries of non-sonic, sonic and commercial LiFePO$_4$ were 269.92; 149.85 and 106.2 Ω, respectively. Meanwhile, the specific capacities at 0.1C of non-sonic, sonic and commercial LiFePO$_4$ were 98.70; 120.17 and 125.23 mAh/g, respectively. As confirmed by SEM image, the particle distribution of sonic-LiFePO$_4$ were more homogenous, and had properties similar to the commercial ones. It is concluded that the sonication procedure carried out prior to hydrothermal has improved performance of the lithium ion battery.

Keywords: Lithium-ion Battery, LiFePO$_4$ cathoda, Sonication, Hydrothermal

ABSTRAK

KARAKTERISASI DAN ELEKTROKIMIA LiFePO$_4$ YANG DISINTESIS DENGAN METODE SONIKASI-HIDROTERMAL. Telah dilakukan sintesis bahan katoda LiFePO$_4$ untuk baterai isi ulang ion-lithium dengan kombinasi sonikasi dan metode hidrotermal. Dengan mereaksikan campuran dari FeSO$_4$.7H$_2$O, H$_3$PO$_4$, LiOH dan etilena glikol. Campuran disonikasi dengan ultrasonik sebelum proses hidrotermal. Hasil sintesis dikarakterisasi masing-masing, struktur kristal dengan difraksi sinar-X (XRD), struktur mikro dengan *Scanning Electron Microscope* (*SEM*), dan sifat listrik dengan Spektroskopi Impedansi (EIS). Dari data X-ray menunjukkan bahwa struktur kristal dari LiFePO$_4$ memiliki grup ruang P m n a (struktur olivin). Ukuran kristal dari sampel LiFePO$_4$ tidak-disonikasi, sonikasi dan komersial masing-masing sebesar 730,2; 3068 dan 639,4 Å. Unjuk kerja sel baterai impedan diukur dengan Spektroskopi Impedansi dan *charge/discharge* dengan *Battery Analyzer BST-8*. Dari data EIS diperoleh hasil impedansi baterai dari bahan LiFePO$_4$ tidak-disonikasi, sonikasi dan komersial masing-masing sebesar 269,92; 149,85 dan 106,2 Ω. Sedang hasil *charge/discharge* pada 0,1C diperoleh kapasitas-spesifik LiFePO$_4$ tidak-disonikasi, sonikasi dan komersial masing-masing sebesar 98,70; 120,17 dan 125,23 mAh/g. Hal ini juga ditunjukkan pada gambar *SEM* bahwa distribusi partikel LiFePO$_4$ hasil sonifikasi lebih homogen dan memiliki sifat yang mirip dengan komersial. Dengan demikian dapat disimpulkan bahwa sonifikasi sebelum hidrotermal telah meningkatkan kinerja baterai ion-lithium.

Kata kunci: Baterai ion-lithium, Katoda LiFePO$_4$, Sonikasi, Hidrotermal

INTRODUCTION

Efficient low cost lithium ion battery methods are currently being developed for large scale manufacturing. Most of the research in lithium ion batteries are focusing on improvement of materials for cathodes and electrolytes for better performance and safety [1-3]. The different methods are researched to show the benefits of using lithium iron phosphate (LiFePO$_4$) as cathode material over other Li-ion based materials such as manganese or cobalt based lithium cathodes. Solid state reaction [4] co-precipitation [5], ball-milling and ball-milling microwave heating [6,7], doping and sol-gel [8] are various techniques being used to synthesize LiFePO$_4$ powders. However, some drawbacks, namely, poor electronic conductivity, low density, and low ionic diffusivity, which have limited its application [9]. The electronic conductivity [10] of LiFePO$_4$ is ~ 10^{-9} S.cm^{-1}, it is much lower than that of LiCoO$_2$ (~10^{-3} S.cm^{-1}) and LiMn$_2$O$_4$ (2×10^{-5}- 5×10^{-5} S.cm^{-1}) [11]. However, LiFePO$_4$ is a good Li ion battery cathode for its high theoretical capacity, cycle/thermal stability, and environmental benefits over other Li ion type batteries. The structure of LiFePO$_4$ is also shown to have an olivine structure providing a safer charging/discharging than other cathode materials. This material shows good theoretical capacity at 170mAh/g and a flat voltage of 3.4 V, but low conductivity is the major disadvantage of these types of cathodes [8,12].

Electronic conductivity of LiFePO$_4$ could be improved by carbon coating metal doping [13,14], and low ionic diffusivity may be improved through reduction of particle size. Previously, it was reported that particle sizes depend on the synthesis method and the media of preparation (pH, pressure, etc.) used [15]. One of the most relevant methods for reducing particle size was the hydrothermal method [16,17]. The hydrothermal method is also a simple method which involves low temperature reaction. The reaction temperature of hydrothermal synthesis of LiFePO$_4$ (LFP) was usually in exceed of 175°C to minimize iron disorder and to obtain material with correct lattice parameters and volume. Sonochemistry or sonication methode is one of the earliest techniques used to prepare nanosized compounds. However, there were no studies that combine both the ultrasonic and hydrothermal methods on synthesizing LiFePO$_4$. Therefore in the present work, the sonication method was performed prior to a hydrothermal process in order to obtain a more homogenous microstructure and better capacities. In order to confirm the crystal structure and microstructure the LiFePO$_4$-sonic was characterized by X-ray diffraction and scanning electron microscope. Furthermore, performance of the battery was analyzed by impedance spectroscopy and battery analyzer. The results were compared with the commercial LiFePO$_4$.

EXPERIMENTAL

Material Preparation

Cathode materials of LiFePO$_4$ were prepared via a sonication-hydrothermal process. The starting materials were FeSO$_4$.7H$_2$O (Sigma-Aldrich, 99.0%), H$_3$PO$_4$ (Aldrich, 85.0%), LiOH (Merck, 98.0%) and ethylene glycol (Merck, 99.5%), with mole ratio 3 : 1 : 1 : 1/3. First LiOH was dissolved in 60 mL of deionized water, H$_3$PO$_4$, FeSO$_4$·7H$_2$O. Ethylene glycol was added subsequently, with stirring to get suspension. In this study a sonication was applied for 30 minutes to homogenize the mixture prior to the hydrotermal process. After sterring and with/ without sonication, the mixed solution was transferred into a 90 mL home made teflon-lined stainless steel autoclave. It was sealed off tightly followed by heating in an electric mufle oven at temperatures of 180°C for 24 hours, then cooled down to room temperature. Details of the hydro thermal method has been described elsewhere [18,19]. The solid grey-green precipitates was filtered and washed several times with ethanol and distilled water and then dried at vacuum oven at 110°C for 10 hrs then heated at 600°C for 6 hrs.

Structural Characterization

For comparison, a commercial powder LiFePO$_4$ was used in the present work. The samples are then labelled as nonsonic-LiFePO$_4$, sonic-LiFePO$_4$ and commercial-LiFePO$_4$. The crystal structure of those LiFePO$_4$ were characterized by X-ray diffraction (XRD) using a PANalytical EMPYREAN Series-2, using Cu Kα, scan range from 10° to 80°. The morphology of the samples was observed by using Scanning Electron Microscopy (SEM, JSM-6510A).

Cathode Preparation

The cathode was prepared by mixing the active materials with artificial carbon and then grounding the mixture for 30 minutes. Polyvinylidene fluoride (PVDF) was dissolved in N-methyl-2-pyrrolidinone (NMP) solution using magnetic stirring and simultaneously heated at 80°C for 2 hours. The weight ratio of active materials with artificial carbon and PVDF was 85:10:5. The slurry was formed in the vacuum mixer for 1h, and the slurry was pasted onto an aluminum current collector using doctor blade. It was dried on oven vacuum at 110 ^{o}C for 10 hrs.

Cell Assembly and Electrochemical Testing

In the present work, three half-cell battery was prepared from LiFePO$_4$ nonsonication-hydrothermal/Li (nonsonic-LiFePO$_4$), sonication-hydrothermal/Li (sonic-LiFePO$_4$) and LiFePO$_4$ commercial/Li (commercial-LiFePO$_4$). All of half-cell battery were constructed inside

an argon filled glove box Vigor with the content of O$_2$ less than 1 ppm. The performance of battery was evaluated in CR2016 coin-type cells, using 20 mm diameter coin cells (CR2016) with Celgard 2500™ separator, Li (reference electrode) and electrolyte (1M LiPF6 dissolved in ethylene carbonate (EC):dimethyl (DMC) 1:2 solution). The crimped coin cells were placed in a stainless steel cell (MTI Corporation) for electrochemical characterization. The impedance spectroscopy was done by LCR Hioki Tester. The charge–discharge experiment was conducted using a battery analyzer system (BTS-8, MTI, 5V/1mA) from 2.5 to 4.2V for several cycles at 0.1C.

RESULTS AND DISCUSION

Materials Characterizations

The crytal structure of nonsonic, sonic and commercial-LiFePO$_4$ powders were analyzed by XRD to verify phase purity. The XRD results were illustrated in Figure1(a), (b) and (c), respectively. In order to analyze the purity of the LiFePO$_4$-sonic, the data was analyzed by using High Score Plus refinement application code. It was clear that the sonication process has increased the crystalinity of the LiFePO$_4$, in comparison to the sample without sonication, with the average of crystallite size of 3068.0 Å. Meanwhile, non-sonic LiFePO$_4$ showed smaller crystallitesizes with the average of 730.2 Å, and higher background scattering.

Figure1(b) and 1(c) showed the comparison of sonic-LiFePO$_4$ and commercial-LiFePO$_4$. It is shown that sonic- LiFePO$_4$ has the identical XRD pattern with the commercial-LiFePO$_4$. It can be seen here, that the dominant diffraction peaks can be indexed as the orthorhombic LiFePO$_4$ phase with space group *Pnma*, according to the standard pattern of JCPDF 016-2282. It means that the synthesized LiFePO$_4$ via sonication-hydrothermal process was successfully formed and the phase was pure 100% LiFePO$_4$. Similar result was observed for LiFePO$_4$-commercial in Figure 1(c), with100% pure LiFePO$_4$. However, by close inspections, it is shown that there was a discrepancy between the sonic-LiFePO$_4$ and commercial-LiFePO$_4$, such as the broadening of the crystalline Bragg peaks. The peaks belong to the sonic-LiFePO$_4$ are much sharper in comparison to the peaks of commercial-LiFePO$_4$. As listed in Table 1, the crystallite sizes were 730.2 Å, 3068 Å and 639 Å for non-sonic, sonic and commercial-LiFePO$_4$, respectively. The microstructures were observed by SEM shown in Figure 2(a),2(b) and 2(c), for nonsonic, sonic and commercial-LiFePO$_4$, respectively. Figure 2(a) showed that the particles of non sonic LiFePO$_4$ was agglomerated and not well distributed.

Similar result was observed for the microstructure of sonic and commercial-LiFePO$_4$. For nonsonic LiFePO$_4$ the particle sizes were not well distributed. The morphologies are rather like hexahedral sheets, which resulted from the anisotropic surface energy of LiFePO$_4$. On the microstructure of an LiFePO$_4$/C composite generated through sonication-hydrothermal showed a more uniform morphology compared with nonsonic-LiFePO$_4$ [20].

Electrochemical Characterizations

Before analyzing the battery performance, it was measured by impedance spectroscopy. The EIS results
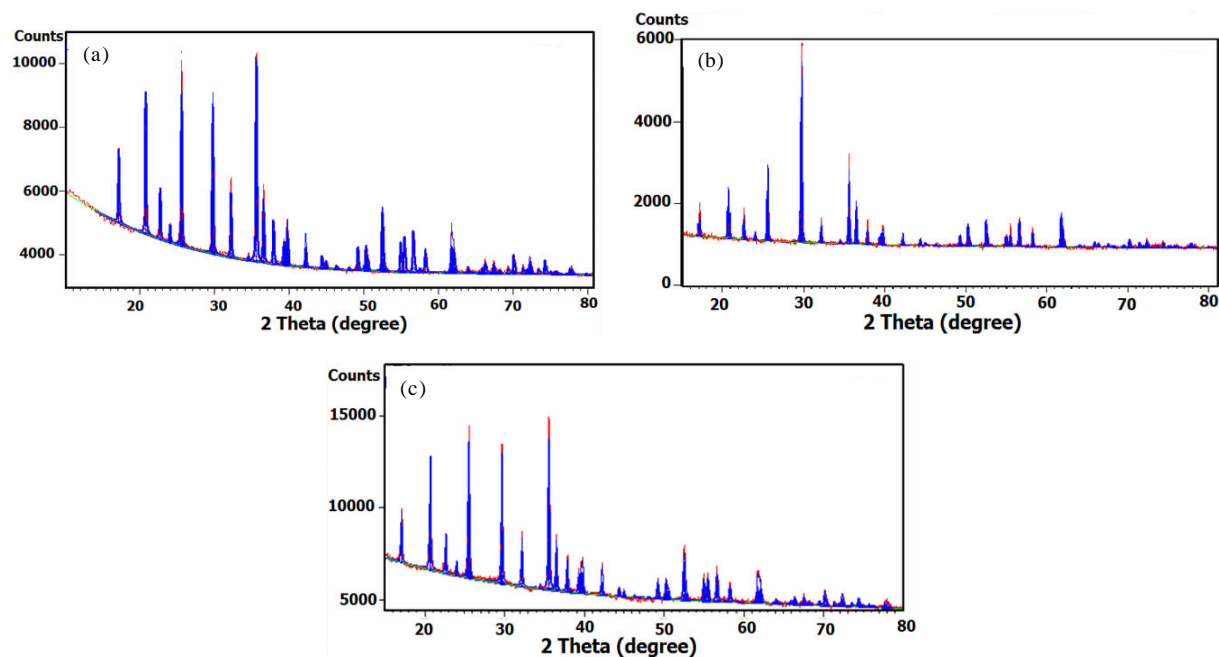

Figure 1. (a). The XRD patterns of (a). nonsonic-LiFePO$_4$ (b). sonic-LiFePO$_4$ and (c). commercial-LiFePO$_4$.
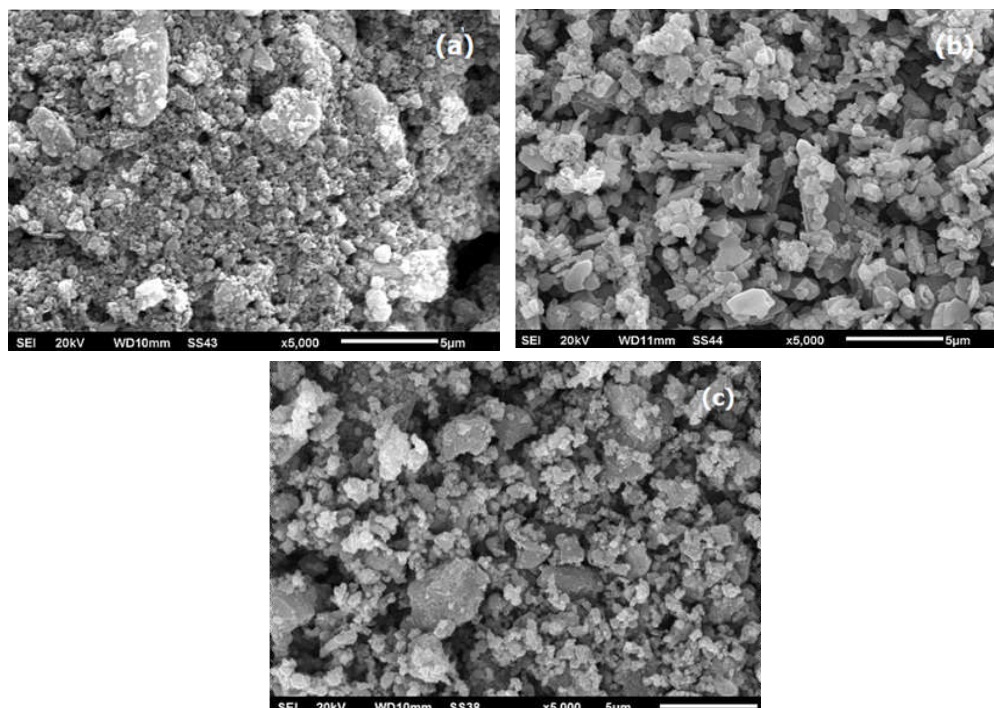
Figure 2. The SEM image of (a). nonsonic-LiFePO$_4$, (b). sonic-LiFePO$_4$ and (c). commercial-LiFePO$_4$

Table 1. Crystal structure analysis of nonsonic, sonic and commercial-LiFePO$_4$

	Nonsonic- hydrothemal	Sonic-hydrothermal	Powder Commercial
Formula /Unit Crystal	Li$_4$Fe$_4$O$_{16}$	Li$_4$Fe$_4$O$_{16}$	Li$_4$Fe$_4$O$_{16}$
Formula mass (g/mol)	631.0376	631.0376	631.0376
Calculate Density (g/cm^3)	3.5892	3.6011	3.6072
Weight Fraction (%)	100	100	100
Space group (No.)	P n m a (62)	P n m a (62)	P n m a (62)
Lattice Parameters :			
a (Å)	10.3295(4)	10.3390(4)	10.3169 (4)
b (Å)	6.0056 (2)	6.0032 (2)	6.0018 (2)
c (Å)	4.7010(2)	4.6921 (2)	4.6908 (2)
FWHM (2Th=35.57°)	0.1665	0.1063	0.1763
alpha (o)	90	90	90
beta (o)	90	90	90
gamma (o)	90	90	90
Preferred Orientation	1.020686		
Parameters and Direction			
[0 01]	0.743721		
[01 0]	0.984201		
[0 1 0]			
Crystallite Size (Å)	730.2	3068.0	639.4
% Strain	0.000	0.028	0.008
Formula /Unit Crystal	Li$_4$Fe$_4$O$_{16}$	Li$_4$Fe$_4$O$_{16}$	Li$_4$Fe$_4$O$_{16}$
Formula mass (g/mol)	631.0376	631.0376	631.0376
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of non-sonic, sonic and commercial- LiFePO$_4$ are shown in Figure 3. The intercept on X-axis in the high frequency region indicates an internal resistance of the cell, and the diameter of the semicircle represents the effect caused by charge transfer and electrochemical double layer. The straight line at a 45° angle after the semicircle represents the resistance in the bulk electrode [21]. From the data shown in Figure 3, it is shown that the impedance of commercial-LiFePO$_4$ was lower than both sonic and nonsonic LiFePO$_4$. However, by close inspection it becomes clear that there was slightly different of resistant between the sonic and commercial-LiFePO$_4$, namely 149.85 Ω and 106.2 Ω, respectively, mean while the non-sonic LiFePO$_4$ was about 269.92 Ω. It means that the
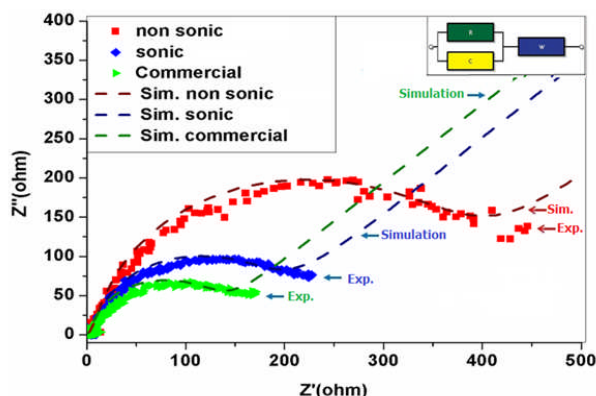
Figure 3. Impedance plots of half cells of non-sonic, sonic and commercial-LiFePO₄/Li

sonic-LiFePO₄ has better electronic conductivity compared to the nonsonic ones (Table 2) [22].

Table 2. Resistance and specific capacities of nonsonic, sonic and commercial.

Battery lithium ion	R (Ω)	W ($\Omega.s^{-2}$)	Specific Capacity (mAh/g)
nonsonic- LiFePO₄ /Li	269.92	1728.2	98.70
sonic-LiFePO₄ /Li	149.85	1128.3	120.17
commercial-LiFePO₄ /Li	106.2	939.61	125.23

The effects of carbonaceous materials on the physical and electrochemical performance of LiFePO₄ are reviewed by Kang Fei-Yu et al [23]. The introduction of an in-situ grown carbon coating would be beneficial to limiting the LiFePO₄ growth and increasing the electric conductivity. The structure and precursors of the in-situ grown carbons have a great influence in the rate performance of the hybrids, which can be related to an improved electron and ion transfer rate. In this case, the addition of ethylene glycol as a carbon source would affect the ionic conductivity and ion transport. Though, the crystal growth could not be limited, due to the sonication prior to hydrothermal process. Furthermore, performance of half-cells of nonsonic, sonic and commercial LiFePO₄ with the counter electrode lithium metal, Li, were analyzed by using battery analyser. Fig.4(a), 4(b) and 4(c) showed charge discharges of nonsonic-LiFePO₄/Li, sonic-LiFePO₄/Li and commercial -LiFePO₄/Li, respectively. The characteristic showed a flat discharge plateau at around 3.2 V, which represents a LiFePO₄ working voltage. The charge discharge processes were done for 10 cycles at 0.1 C.

The spesific capacity of lithium ion battery made from nonsonic and sonic-LiFePO₄ were 98.7 and 120.17 mAh/g, respectively, meanwhile from commercial LiFePO₄ was 125.23 mAh/g, at 0.1C. It is concluded that the sonication prior to hydrothermal has improved performance of the lithium ion battery or similar performance as the commercial ones.

In order to achieve an excellent electrochemical performance of LiFePO₄, it is necessary to take advantage
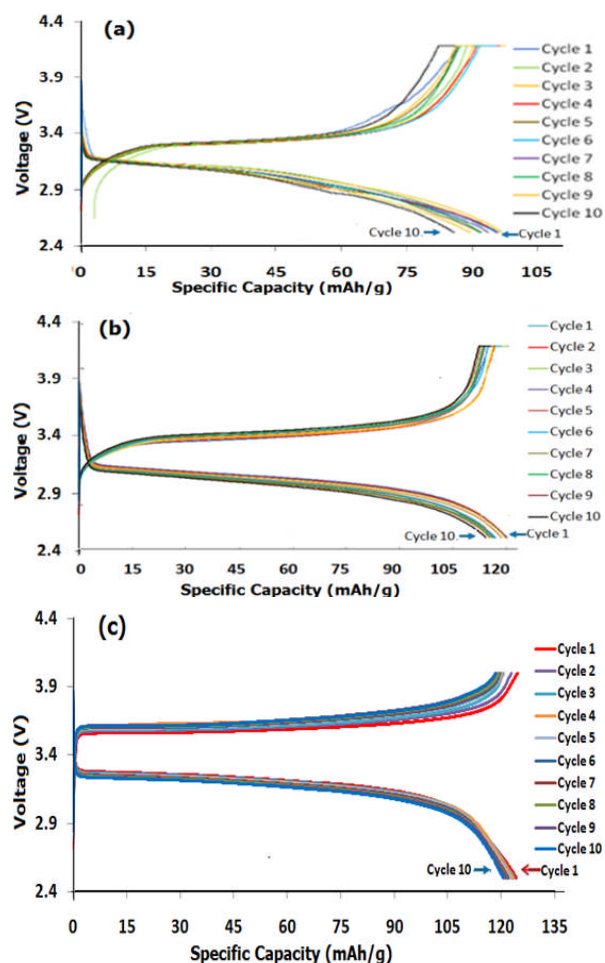
Figure 4. (a). Specific capacity of (a). nonsonic-LiFePO₄/Li, (b). sonic-LiFePO₄/Li and (c). commercial-LiFePO₄/Li.

of and to combine these approaches to optimize electron and ion transfer rates. Also, it is most important to minimize the carbon content in LiFePO₄ carbon hybrids to increase volumetric energy density. The primary particle size that determines electrochemical performance, including cycling, rate capability, and low-temperature performance, could be successfully controlled via this method.

The cyclic performances after 10th cycles for nonsonic, sonic and commercial-LiFePO₄/Li were shown in Fig. 5 to observe its capacity retentions. The nonsonic-LiFePO₄/Li showed the first discharge at 98.70 mAh/g then decreased to 81.16 mAh/g after 10th cycles or decreased about 17.7%. The sonic-LiFePO₄/Li showed the first discharge at 120.17 mAh/g then decreased to 114.26 mAh/g after 10th cycles or decreased about 4.90%. For the commercial LiFePO₄/Li, the first discharge at 125.23 mAh/g and decreased to 120.64 mAh/g for the 10th cycles which was about 3.70%. The capacity retentions of the sonic- LiFePO₄ is rather similar to the commercial ones. It is shown that the sonication prior to hydrothermal process improved performance of the lithium ion batteries.
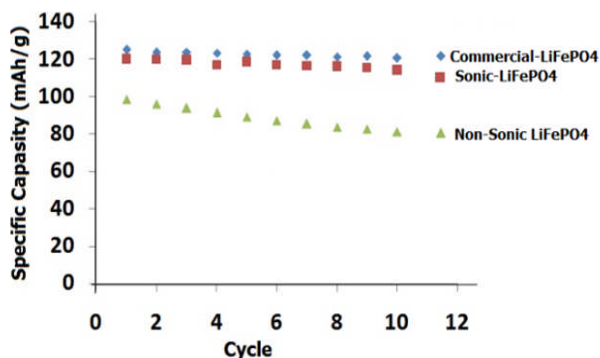
Figure 5. Cycling performance of nonsonic, sonic and commercial-LiFePO₄/Li.

CONCLUSION

LiFePO$_4$ as cathode material for Li-ion battery was successfully synthesized by sonication-hydrothemal method. The addition of ethylene glycol during sonication had increased the electronic conductivity since it became a source of carbon. The charge–discharge results show that both sonic and commercial-LiFePO$_4$ showed good performance of the lithium ion battery, but the specific capacity was slightly higher for commercial LiFePO$_4$. In this case, the highest spesific capacity obtained for sample prepared by sonication-hydrothermal was 120.70 mAh/g, while from commercial was 125.23 mAh/g at 0.1C. It was assumed that the crystallite sizes as the results of the hydrothermal process had affected performance of the electrical conductivity and also the battery. The sonication prior to hydrothermal has also proved the growth of the LiFePO$_4$ crystal more homogenous due to smaller particles of the raw material mixtures. It is concluded that the sonication prior to hydrothermal has improved performance of the lithium ion battery.

For further study, it is important to understand the temperature effect of sonication-hydrothermal methods for the nucleation rate of the LiFePO$_4$ crystal. The primary particle size that determines electrochemical performance, including, rate capability, and low temperature performance, could be successfully controlled via this method. Hence, this would be the most promising method for commercial production of LiFePO$_4$/C directed to hybrid electrical vehicles and pure electrical vehicle market.

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