Synthesis of LiFePO$_4$/Li$_2$SiO$_3$/reduced Graphene Oxide (rGO) Composite via Hydrothermal Method

M Arifin$^1$, F Iskandar$^{1,2,*}$, A H Aimon$^1$, M M Munir$^1$ and B W Nuryadin$^3$

$^1$Department of Physics, Institut Teknologi Bandung, 40132 Bandung, Indonesia
$^2$Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, 40132 Bandung, Indonesia
$^3$Department of Physics, Faculty of Science and Technology, UIN Sunan Gunung Djati, 40614 Bandung, Indonesia

*E-mail: ferry@fi.itb.ac.id

Abstract. LiFePO$_4$ is a type of cathode active material used for lithium ion batteries. It has a high electrochemical performance. However, it suffers from certain disadvantages such as a very low intrinsic electronic conductivity and low ionic diffusion. This study was conducted to increase the conductivity of LiFePO$_4$. We have investigated the addition of Li$_2$SiO$_3$ and reduced graphene oxide (rGO) to LiFePO$_4$. The objective of this research was to synthesize LiFePO$_4$/Li$_2$SiO$_3$/rGO via hydrothermal method. Fourier transform infrared spectroscopy (FTIR) measurement showed that the peaks corresponded to the vibration of LiFePO$_4$. Further, X-ray diffraction (XRD) measurement confirmed a single phase of LiFePO$_4$. Finally, scanning electron microscopy (SEM) images showed that rGO was distributed on the LiFePO$_4$/Li$_2$SiO$_3$ structure.

1. Introduction

Many researchers are interested in the optimization of LiFePO$_4$ as cathode active material for lithium ion batteries [1]. This material has several advantages, such as low toxicity, cheap, long cycle ability, and high safety [2]. It also has high electrochemical performance, such as a stable operational voltage at 3.45 V and high theoretic capacity at 170 mAh.g$^{-1}$. However, it suffers from certain disadvantages such as very low intrinsic electronic conductivity and low lithium ionic diffusion [3]. To counter these problems, several researchers have attempted to improve the electrical conductivity and ionic diffusion of LiFePO$_4$ with controlled morphology [4] or composites of LiFePO$_4$ [5].

Reduced graphene oxide (rGO) and Li$_2$SiO$_3$ are materials with high electrical [6] and ionic conductivity [7], respectively. With its high electrical conductivity, rGO can increase electrical conductivity of LiFePO$_4$. Meanwhile, with its high ionic conductivity, Li$_2$SiO$_3$ can improve ionic diffusion of LiFePO$_4$. Therefore, the objective of this research was to composite Li$_2$SiO$_3$ and rGO into LiFePO$_4$ using a hydrothermal process.
2. Experimental Procedure

2.1. Materials Preparation

Reduced Graphene Oxide (rGO) was synthesized by chemical method. Firstly, graphite oxide was synthesized from graphite fine powder (Aldrich) using the Marcano method [8]. Afterwards, the prepared graphite oxide was exfoliated and dispersed in ethylene glycol (C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}, Merck) by ultrasonication to form a graphene oxide (GO) suspension. Hydrazine hydrate (N\textsubscript{2}H\textsubscript{4}, Merck) was then added to the above suspension and the resulting mixture was heated using microwave-assisted heating at 300 W for 20 minutes [9]. Finally, the chemically reduced product was filtered, washed and dried in an oven at 60 °C for 12 hours. The product is called reduced graphene oxide (rGO).

LiFePO\textsubscript{4}/Li\textsubscript{2}SiO\textsubscript{3}/rGO composite was prepared via hydrothermal method with the molar ratios of lithium hydroxide (LiOH, Merck), phosphoric acid (H\textsubscript{3}PO\textsubscript{4}, 85%, Merck), and iron (II) sulfate heptahydrate (FeSO\textsubscript{4}·7H\textsubscript{2}O, Merck) at 3:1:1, and the molar ratios of LiOH and SiO\textsubscript{2} at 2:1. Specifically, distilled water and citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}, Merck) were mixed to form a citric acid solution. 0.083 g SiO\textsubscript{2} was mixed with 0.3 M LiOH aqueous solution (in the citric acid solution), which partly formed Li\textsubscript{2}SiO\textsubscript{3} and then rGO (1 wt% of the obtained LiFePO\textsubscript{4}), which was ultrasonically dispersed in distilled water. This mixture was mixed with 0.1 M H\textsubscript{3}PO\textsubscript{4} to form a white suspension of Li\textsubscript{3}PO\textsubscript{4}. Subsequently, 0.1 M of FeSO\textsubscript{4}·7H\textsubscript{2}O aqueous solution was added to the suspension. The obtained precursor was then transferred into a 500-ml teflon-lined stainless steel autoclave equipped with a magnetic stirrer. The mixing process in the autoclave was carried out under nitrogen atmosphere and maintained stirring at 180 °C for 5 hours. After being cooled to room temperature, the produced sample was filtered and dried at 80 °C for 2 hours. After being cooled to ambient temperature, LiFePO\textsubscript{4}/Li\textsubscript{2}SiO\textsubscript{3}/rGO composite (without rGO) was also prepared under the same conditions.

2.2. Characterization

All the samples were characterized by Fourier transform infrared spectroscopy (FTIR) using an Alpha FTIR Spectrometer Bruker 1176 396 and X-ray diffraction (XRD) using an XRD Philips Analytical PW 1710 BASED with a step size of 0.02° for Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscope (SEM) measurements were carried out on a field emission scanning electron microscope (Jeol JCM-6000 Benchtop SEM, Japan).

3. Results and discussion

Reduced graphene oxide (rGO) was synthesized via the Marcano method using a hydrazine hydrate as reducing agent and microwave-assisted heating [9]. The FTIR spectra show that there were vibrations at wavenumbers of 1116 cm\textsuperscript{-1}, 1228 cm\textsuperscript{-1}, 1414 cm\textsuperscript{-1}, 1622 cm\textsuperscript{-1}, 1735 cm\textsuperscript{-1} [10], and 3223 cm\textsuperscript{-1}, as shown in Figure 1(a).

![Figure 1. FTIR spectra of (a) GO and (b) rGO.](image-url)
The peaks shown in Figure 1(a) are the functional groups of graphene oxide (GO), i.e. C-O (1116 cm\(^{-1}\)), epoxy C-O (1228 cm\(^{-1}\)), carboxyl C-O (1414 cm\(^{-1}\)), aromatic C-C/C=C (1622 cm\(^{-1}\)), carbonyl C=O (1731 cm\(^{-1}\)), and O-H (3223 cm\(^{-1}\)) [10]. After reduction, the peaks of the oxygen functional groups were reduced significantly, as shown in Figure 1(b).

Figure 2 shows the FTIR spectra of LiFePO\(_4\)/Li\(_2\)SiO\(_3\) and LiFePO\(_4\)/Li\(_2\)SiO\(_3\)/rGO. There are vibration peaks at 548 cm\(^{-1}\), 577 cm\(^{-1}\), 857 cm\(^{-1}\), 945 cm\(^{-1}\), 1051 cm\(^{-1}\), and 1138 cm\(^{-1}\). The peaks at wavenumbers 945 cm\(^{-1}\) and 1138 cm\(^{-1}\) correspond to the symmetric stretching vibrations \(v_1\) of P-O, while the big peak at 1051 cm\(^{-1}\) is specific to the intramolecular antisymmetric stretching vibrations \(v_3\) of P-O. Antisymmetric bending vibrations \(v_4\) of O-P-O were found at 548 cm\(^{-1}\). Furthermore, the peaks centered at 577 cm\(^{-1}\) and 635 cm\(^{-1}\) can be attributed to the intramolecular symmetric stretching of Fe-O bonds in FeO\(_6\) units. The number and positions of the bands correspond to vibration of LiFePO\(_4\) [11]. The peak at wavenumber 857 cm\(^{-1}\) corresponds to vibration of Li\(_2\)SiO\(_3\) [12]. Meanwhile, the bands that relate to rGO did not appear due to the low concentration of rGO in the LiFePO\(_4\)/Li\(_2\)SiO\(_3\)/rGO composite.

![Figure 2. The FTIR spectra of LiFePO\(_4\)/Li\(_2\)SiO\(_3\) and LiFePO\(_4\)/Li\(_2\)SiO\(_3\)/rGO.](image)

The XRD patterns of LiFePO\(_4\)/Li\(_2\)SiO\(_3\) and LiFePO\(_4\)/Li\(_2\)SiO\(_3\)/rGO are shown in Figure 3. All patterns exhibit single phase of LiFePO\(_4\) with an ordered olivine structure based on JCPDS 81-1173 [13].

![Figure 3. XRD patterns of LiFePO\(_4\)/Li\(_2\)SiO\(_3\) and LiFePO\(_4\)/Li\(_2\)SiO\(_3\)/rGO.](image)
The diffraction peak intensity indicates the crystal quality of the prepared LiFePO$_4$. There are no obvious diffraction peaks of Li$_2$SiO$_3$ and rGO due to the amorphous structure and its low content in the composite. Moreover, the peak intensities of the LiFePO$_4$/Li$_2$SiO$_3$/rGO composite are slightly higher than the peaks intensities of LiFePO$_4$/Li$_2$SiO$_3$. This indicates that the crystallite size of the LiFePO$_4$/Li$_2$SiO$_3$/rGO composite was bigger than the crystallite size of LiFePO$_4$/Li$_2$SiO$_3$. As a result, the addition of rGO can improve the crystallite size of LiFePO$_4$/Li$_2$SiO$_3$/rGO composite.

Figure 4. The SEM images of (a) LiFePO$_4$/Li$_2$SiO$_3$, (b) LiFePO$_4$/Li$_2$SiO$_3$/rGO, and (c) rGO [9].

Reduced graphene oxide (rGO) in the compound was identified by SEM. The SEM images show that rGO was distributed in the LiFePO$_4$/Li$_2$SiO$_3$ structure as shown in Figure 4. The images also reveal that the particles were in agglomerate formation.

4. Conclusion

In this study, LiFePO$_4$/Li$_2$SiO$_3$/rGO composite was successfully prepared by hydrothermal method. FTIR measurement showed the vibration peaks of LiFePO$_4$/Li$_2$SiO$_3$. Further, the XRD patterns confirmed single phase of LiFePO$_4$. However, there were no obvious diffraction peaks of Li$_2$SiO$_3$ and rGO due to its low content in the structure. Finally, the SEM images confirmed rGO distribution in the LiFePO$_4$/Li$_2$SiO$_3$ structure.

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