

Synthesis of LiFePO₄/Li₂SiO₃/reduced Graphene Oxide (rGO) Composite via Hydrothermal Method

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Abstract. LiFePO₄ 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 LiFePO₄. We have investigated the addition of Li₂SiO₃ and reduced graphene oxide (rGO) to LiFePO₄. The objective of this research was to synthesize LiFePO₄/Li₂SiO₃/rGO via hydrothermal method. Fourier transform infrared spectroscopy (FTIR) measurement showed that the peaks corresponded to the vibration of LiFePO₄/Li₂SiO₃. Further, X-ray diffraction (XRD) measurement confirmed a single phase of LiFePO₄. Finally, scanning electron microscopy (SEM) images showed that rGO was distributed on the LiFePO₄/Li₂SiO₃ structure.

1. Introduction

Many researchers are interested in the optimization of LiFePO₄ 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 LiFePO₄ with controlled morphology [4] or composites of LiFePO₄ [5].

Reduced graphene oxide (rGO) and Li₂SiO₃ are materials with high electrical [6] and ionic conductivity [7], respectively. With its high electrical conductivity, rGO can increase electrical conductivity of LiFePO₄. Meanwhile, with its high ionic conductivity, Li₂SiO₃ can improve ionic diffusion of LiFePO₄. Therefore, the objective of this research was to composite Li₂SiO₃ and rGO into LiFePO₄ 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 Marciano method [8]. Afterwards, the prepared graphite oxide was exfoliated and dispersed in ethylene glycol ($C_2H_6O_2$, Merck) by ultrasonication to form a graphene oxide (GO) suspension. Hydrazine hydrate (N_2H_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).

$LiFePO_4/Li_2SiO_3/rGO$ composite was prepared via hydrothermal method with the molar ratios of lithium hydroxide (LiOH, Merck), phosphoric acid (H_3PO_4 , 85%, Merck), and iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Merck) at 3:1:1, and the molar ratios of LiOH and SiO_2 at 2:1. Specifically, distilled water and citric acid ($C_6H_8O_7$, Merck) were mixed to form a citric acid solution. 0.083 g SiO_2 was mixed with 0.3 M LiOH aqueous solution (in the citric acid solution), which partly formed Li_2SiO_3 and then rGO (1 wt% of the obtained $LiFePO_4$), which was ultrasonically dispersed in distilled water. This mixture was mixed with 0.1 M H_3PO_4 to form a white suspension of Li_3PO_4 . Subsequently, 0.1 M of $FeSO_4 \cdot 7H_2O$ 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, $LiFePO_4/Li_2SiO_3/rGO$ composite was obtained. As a reference, $LiFePO_4/Li_2SiO_3$ 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 1 176 396 and X-ray diffraction (XRD) using an XRD Philips Analytical PW 1710 BASED with a step size of 0.02° for Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). 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 Marciano 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^{-1} , 1228 cm^{-1} , 1414 cm^{-1} , 1622 cm^{-1} , 1735 cm^{-1} [10], and 3223 cm^{-1} , as shown in Figure 1(a).

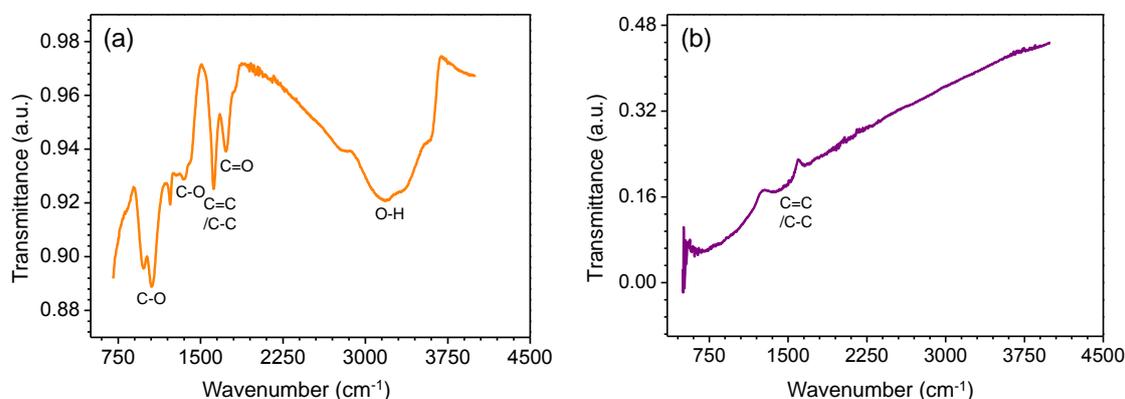


Figure 1. FTIR spectra of (a) GO and (b) rGO.

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 $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$ and $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$. 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 ν_1 of P-O, while the big peak at 1051 cm^{-1} is specific to the intramolecular antisymmetric stretching vibrations ν_3 of P-O. Antisymmetric bending vibrations ν_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_2SiO_3 [12]. Meanwhile, the bands that relate to rGO did not appear due to the low concentration of rGO in the $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$ composite.

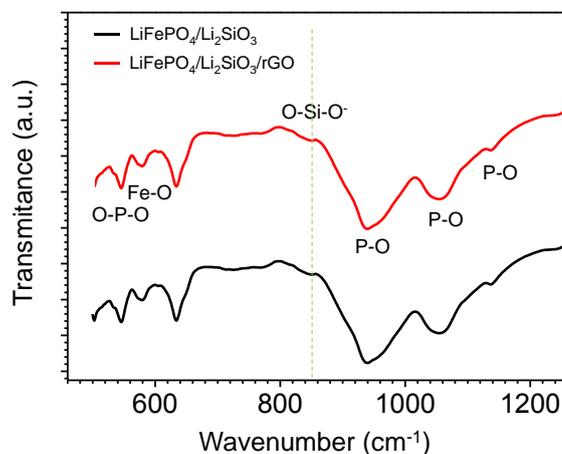


Figure 2. The FTIR spectra of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$ and $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$.

The XRD patterns of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$ and $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$ are shown in Figure 3. All patterns exhibit single phase of LiFePO_4 with an ordered olivine structure based on JCPDS 81-1173 [13].

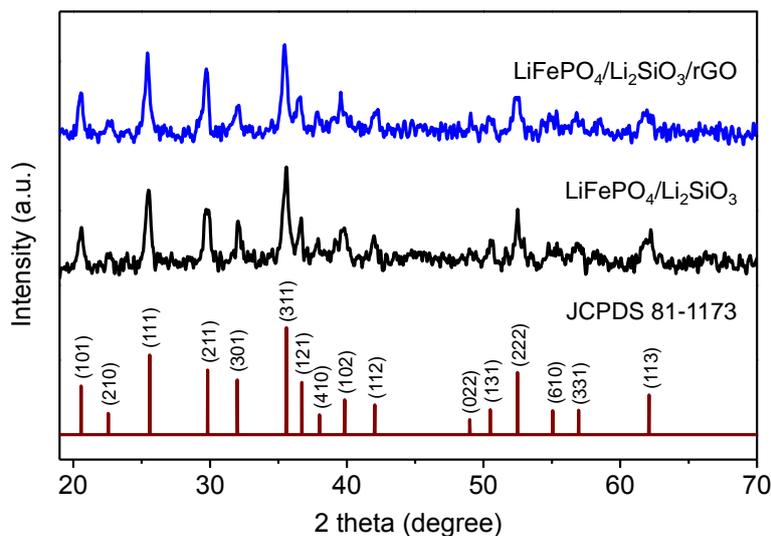


Figure 3. XRD patterns of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$ and $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$.

The diffraction peak intensity indicates the crystal quality of the prepared LiFePO_4 . There are no obvious diffraction peaks of Li_2SiO_3 and rGO due to the amorphous structure and its low content in the composite. Moreover, the peak intensities of the $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$ composite are slightly higher than the peaks intensities of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$. This indicates that the crystallite size of the $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$ composite was bigger than the crystallite size of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$. As a result, the addition of rGO can improve the crystallite size of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$ composite.

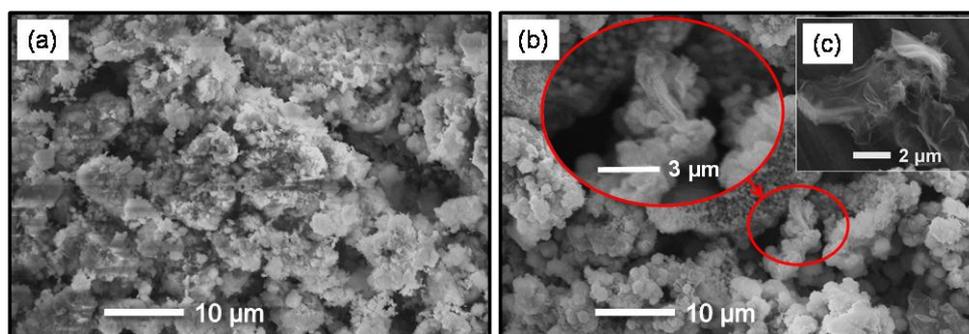


Figure 4. The SEM images of (a) $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$, (b) $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$, and (c) rGO [9].

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

4. Conclusion

In this study, $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3/\text{rGO}$ composite was successfully prepared by hydrothermal method. FTIR measurement showed the vibration peaks of $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$. Further, the XRD patterns confirmed single phase of LiFePO_4 . However, there were no obvious diffraction peaks of Li_2SiO_3 and rGO due to its low content in the structure. Finally, the SEM images confirmed rGO distribution in the $\text{LiFePO}_4/\text{Li}_2\text{SiO}_3$ structure.

Acknowledgements

The authors would like to thank the Indonesia Endowment Fund from the Ministry of Finance Republic Indonesia and the *Desentralisasi* Program from the Ministry of Research, Technology and Higher Education of Republic Indonesia for the financial year of 2015.

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