

Effect of Firing Temperature on the Electrochemical Performance of Nanocapsule-like

LiMn_{0.5}Fe_{0.5}PO₄/C Cathode Materials for Li-Ion Batteries

ผลของอุณหภูมิในการเผาต่อสมบัติทางไฟฟ้าเคมีของวัสดุแคโทด LiMn_{0.5}Fe_{0.5}PO₄/C ที่มีโครงสร้าง
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ABSTRACT

Olivine LiMn_xFe_{1-x}PO₄ cathode materials received high structural and chemical stabilities and high voltage. However, their major disadvantage is low electrical conductivity. In this article, effects of firing temperature that influences the structural, morphological, and electrochemical properties of LiMn_xFe_{1-x}PO₄ and carbon composites have been investigated. X-ray diffraction technique was used to show that the LiMn_xFe_{1-x}PO₄ materials were successfully synthesized by a solvothermal method. Scanning electron microscopy was used to show that the materials were in the nanometer size scale and had capsule-like morphology consisting of the LiMn_xFe_{1-x}PO₄/C nanocrystals distributed in the continuous carbon matrix leading to high electrical conductivity. Raman spectroscopy was used to study the crystallinity of the carbon phase and showed that the material fired at 600 °C provided the highest degree of graphitization. The graphite formation in a combination of the capsule-like nanostructures lead to high charge / discharge capacities of these materials. The highest discharge capacity is found to be 154 mAh.g⁻¹ at a C/10 rate and was resulted from the sample fired at 600 °C for 6h.

บทคัดย่อ

วัสดุแคโทด LiMn_xFe_{1-x}PO₄ เป็นวัสดุที่มีความเสถียรสูงและมีค่าศักย์ไฟฟ้าที่สูง แต่มีข้อเสีย คือ มีความนำไฟฟ้าที่ต่ำ ในบทความนี้ได้ศึกษาผลกระทบของอุณหภูมิในการเผาที่มีอิทธิพลกับคุณสมบัติทางไฟฟ้าเคมีของวัสดุ LiMn_{0.5}Fe_{0.5}PO₄ คอมโพสิตกับวัสดุคาร์บอน จากการตรวจสอบด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ พบว่าวัสดุนี้สามารถถูกสังเคราะห์ด้วยวิธี solvothermal ได้สำเร็จ โดยภาพถ่ายจากกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดพบว่าวัสดุมีขนาดอนุภาคระดับ 100 นาโนเมตร และมีรูปร่างคล้ายแคปซูล ที่ประกอบขึ้นจากผลึกนาโนของวัสดุ LiMn_xFe_{1-x}PO₄/C ที่กระจายตัวอยู่ในเมทริกซ์ของวัสดุคาร์บอนอีกชั้นหนึ่ง จากผลการวิเคราะห์ด้วยเทคนิครามานสเปกโตรสโกปีพบว่าที่อุณหภูมิในการเผา 600 องศาเซลเซียส คาร์บอนที่เคลือบมีความเป็นผลึกมากที่สุด และนำไปสู่ผลการอัดประจุ/คายประจุของวัสดุมีความจุขณะคายประจุสูงถึง 154 mAh.g⁻¹ ที่อัตราการอัดประจุ C/10 (10 ชั่วโมง)

Keywords: LiMn_{0.5}Fe_{0.5}PO₄ composite material, Carbon coating, Raman spectroscopy

คำสำคัญ: วัสดุคอมโพสิต LiMn_{0.5}Fe_{0.5}PO₄ การเคลือบด้วยคาร์บอน รามานสเปกโตรสโกปี

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Introduction

Lithium-ion batteries (LIBs) are one of the key technologies that enable consistent and continuous electrical power for users since the beginning of their existence in 1997. LIBs constituted an essential power sources for portable electronic devices such as laptop computers, cellular phones, digital cameras, and electric vehicles because of their advantage of high energy density. Olivine-typed LiMPO_4 compounds ($M = \text{Co}, \text{Fe}, \text{Mn}, \text{Ni}$) are one of the most studied cathodes in the battery community because they have shown good charge/discharge characteristics, good capacity, and high voltages (3.4 V for Fe, 4.2 V for Mn, 4.8 V for Co, and 5.1 V for Ni). However, Co and Ni compounds toxic and expensive, respectively. Therefore, LiMnPO_4 and LiFePO_4 are more attractive among of all of the olivine-type cathode materials. Of these two, the latter, LiFePO_4 , was heavily investigated and now is one of the most widely used materials in LIBs due to its simple synthesis, environmental friendliness, high theoretical capacity (170 mAh.g^{-1}), and low cost (Padhi et al., 1997; Yamada et al., 2001). However, it is well established that LiFePO_4 has poor electrical conductivity and carbon coating is a common method used with this material to increase its electrical conductivity. Among the LiMPO_4 compounds studied, LiFePO_4 shows a lower voltage, about 3.4 V vs. Li^+/Li . If the voltage of the cathode is increased, the overall energy density of the LIBs using this cathode material will be increased. The main objective of this work to increase the voltage and electrical conductivity of LiFePO_4 by a combination of carbon coating and partially replacing iron ions (Fe^{2+}) with manganese ions (Mn^{2+}) to form $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ compounds. Mn^{2+} can raise the voltage of the LiFePO_4 compound because the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple normally occurs at a higher voltage of 4.1 V vs Li^+/Li while the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple occurs at a voltage of only about 3.4 V vs Li^+/Li (Padhi et al., 1997; Yamada et al., 2001).

The $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4/\text{C}$ compound where $x = 0.5$, was found to be the most suitable for high specific capacity as well as high rate capability, and this material been extensively studied in recent years. Many preparation techniques were used to synthesize $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ materials such as a hydrothermal method (Avenidaño et al., 2014; Xiang et al., 2015), a coprecipitation method (Min Oh et al., 2011; Xiang et al., 2015; Xiang et al., 2016), a sol-gel method (Liu et al., 2017), solid state method (Yamada et al., 2001; Zaghbi et al., 2008; Zong et al., 2013; Liu et al., 2014; Li et al., 2015), and a spray drying method (Chen Yang et al., 2016). Recently, a solvothermal method was introduced to synthesize this material (Saravanan et al., 2011; Huang et al., 2013; Di Lecce et al., 2015; Yuan Yan et al., 2015; Kosova et al., 2018) due to the ability to control the synthesis conditions to form various morphological structures with improved electrochemical performance. For example, Yuan Yan et al. (2015) showed that a nano-sponge materials could deliver a discharge capacity of 150 mAh.g^{-1} at a C/10 rate using a carbon-coating of 15 wt.%. Kosova et al. (2018) reported that a material with hexagonal nano-plates morphology gave a discharge capacity of 97 mAh.g^{-1} at a C/10 rate by using a carbon-coating of up to 20 wt.%. As can be seen, this material can have promising electrochemical performance but still requires a high degree of carbon coating.

In this article, we report of our successful synthesis of a new nanostructured $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ material having a capsule-like morphology comprised of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ nanocrystals homogeneously distributed in the continuous carbon matrix using a solvothermal method. The amount of carbon used in this material was about 5-10 wt.%, which is much lower than reported in previous studies. The effect of firing temperatures on the crystal structure, morphology, and carbon

molecular bonding structure of these materials was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. The results were used to explain the improved electrochemical performance of this material.

Objectives of the study

The aim of this research was to study the influence of firing temperature on the electrochemical properties of the capsule-like nanostructures of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (LMFP)/C cathode materials for lithium-ion batteries.

Methodology

Preparation of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$

Materials: $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (LMFP) powder was synthesized by solvothermal method (depicted in Fig. 1) using a mixture of ethanediol (EG)-and de-ionized water (DI) as a solvent. Lithium hydroxide monohydrate, $\text{LiOH}\cdot\text{H}_2\text{O}$ (98% purity, Sigma-Aldrich), manganese (II) sulfate monohydrate, $\text{MnSO}_4\cdot\text{H}_2\text{O}$ (99% purity, QR&C), iron (II) sulfate heptahydrate, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (99.5% purity, QR&C), and orthophosphoric acid, H_3PO_4 (85% purity, Ajax Finechem) in a Li:Mn:Fe:PO₄ molar ratio of 3:0.5:0.5:1 were dissolved in the EG-DI solvent (4:1 by volume). LiOH was dissolved in EG to form Solution A, while $\text{MnSO}_4\cdot\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and glucose were dissolved in DI water with sonication for 1 h to form Solution B under an Argon gas environment. Then, H_3PO_4 was slowly dropped into Solution B under slowly with stirring for 10 mins. Next, Solutions A and B were stirred together for 10 mins and transferred into a 50 ml Teflon-line stainless steel autoclave under Argon gas environment. The mixture was heat-treated to 185 °C for 18 h to yield crystalline $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ particles. After that the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ particles were centrifuged and vacuum-dried at 80 °C overnight. The obtain particles were mixed with 5 wt.% glucose in DI water with sonication for 30 mins. The mixture was freeze-dried at -48 °C overnight. The collected powders were calcined at 300 °C for 6 h followed by firing at 500 °C (LMFP_500 °C), 600 °C (LMFP_600 °C), and 700 °C (LMFP_700 °C) for 6 h with a heating rate of 5 °C/min under an Ar gas atmosphere.

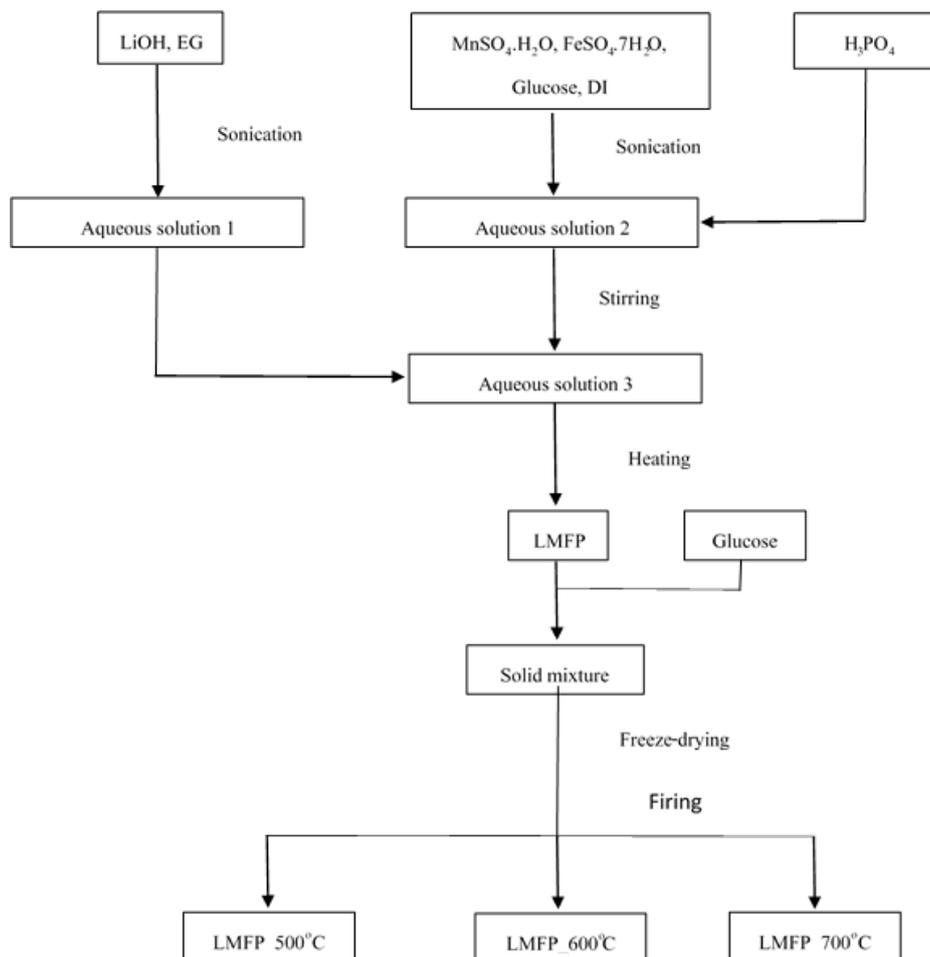


Fig. 1 Flow chart of synthesis process for fabrication of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$, LMFP_500°C, 600°C and 700°C.

Characterization

The crystalline phase of the synthesized samples was examined using an X-ray diffraction (XRD) analyzer (EMPYREAN, PANalytical) over a 2θ range of $10^\circ - 80^\circ$ at a scan rate 10° per min with a step size of 0.02° . The morphology, particle size, and particle size distribution of the samples were observed with scanning electron microscopy (SEM) (Zeiss, Auriga), and the crystalline carbon coating was investigated using Raman spectroscopy. The equipment used in this portion of the study is located in the Research Instrument Center, Khon Kaen University, Thailand.

Electrode preparation and measurement

Each of the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ powders was mixed with conductive carbon black (Super P), and polyvinylidene fluoride (PVdF) as a binder in a weight ratio of 73:13:14 using 1-methyl-2-pyrrolidone (NMP) as a solvent. The slurry was coated on an aluminum foil current collector and dried in a vacuum oven at 80°C overnight before use as electrodes. Then, the dried electrodes were punched into circular dishes and compressed with hydraulic pressure of 20 kPa. The apparatus was assembled using a coin-typed cell (CR2032), using lithium metal as the negative electrode, the dried circular electrode as a cathode, and a bi-layer PE/PP membrane (Celgard) as a separator. The electrolyte consisted of 1 M LiPF_6 dissolved in dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), ethylene carbonate (EC) in a 1:1:1 volume ratio. The cells were assembled in a glove box under an Ar gas atmosphere.

The electrochemical properties of the cells were investigated by using a battery testing system (Austin, TX, USA), at a charge/discharge rate of $C/10$ between 2.2 V to 4.6 V.

Results and Discussion

Characterization of the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$

Fig. 2 shows XRD patterns of the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ powders after firing at 500 °C, 600 °C, and 700 °C for 6 h. After comparing diffraction peaks with the reference pattern of pure olivine-type crystalline material (PDF# 00-011-0456), all samples showed only the diffraction peaks of the orthorhombic structure with Pnma space group of the $\text{LiFePO}_4\text{-LiMnPO}_4$ solid solution. This result confirms that pure phase olivine-type $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ materials were successfully synthesized by the solvothermal method.

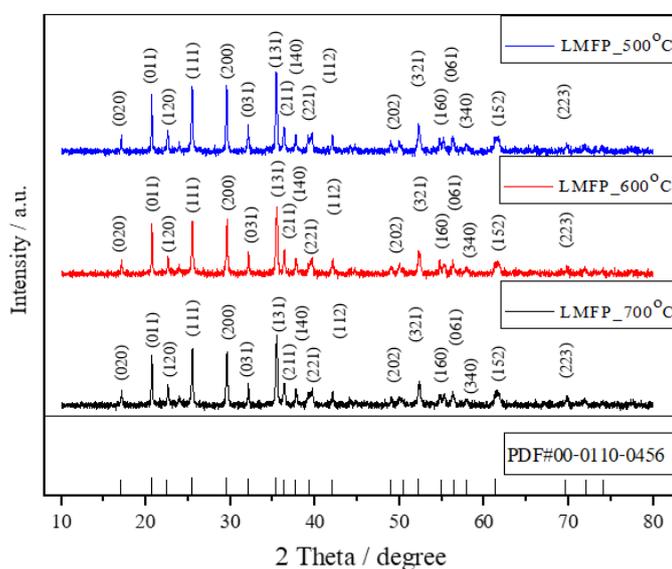


Fig. 2 XRD patterns of the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ powders after firing at 500 °C, 600 °C and 700 °C, respectively.

Fig. 3 shows typical SEM images of the $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ powders synthesized at 500 °C, 600 °C and 700 °C, respectively. As can be seen, all samples show a capsule-like morphology with approximate dimensions of 100 ± 20 nm (length) and 50 ± 20 nm (width). Each of the capsule-like particle consists (Fig. 4b and 4c) of several carbon-coated $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ nanocrystals (Fig. 4a) formed inside a continuous matrix of carbon as is represented in the schematic drawing in Fig. 4. This special morphology should have a positive impact on the electrochemical performance of this material, as is discussed below. At the two lower temperatures, 500 °C and 600 °C, the capsule-like particles are quite homogeneous with a narrow particle size distribution. The sample fired at 600 °C has slightly more uniform nanostructures than the sample fired at 500 °C. As the firing temperature was increased to 700 °C, the particles became broken, with slightly increasing particles size to around 100-120 nm. Agglomerated nanocrystals appear to be expose outside of the continuous carbon matrix (as represented by Fig. 4c) which will had a negative impact on the electrochemical properties of this sample. Therefore, firing temperature has an influence on the morphology of the capsule-like $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ materials, and impacted the electrochemical properties of these materials.

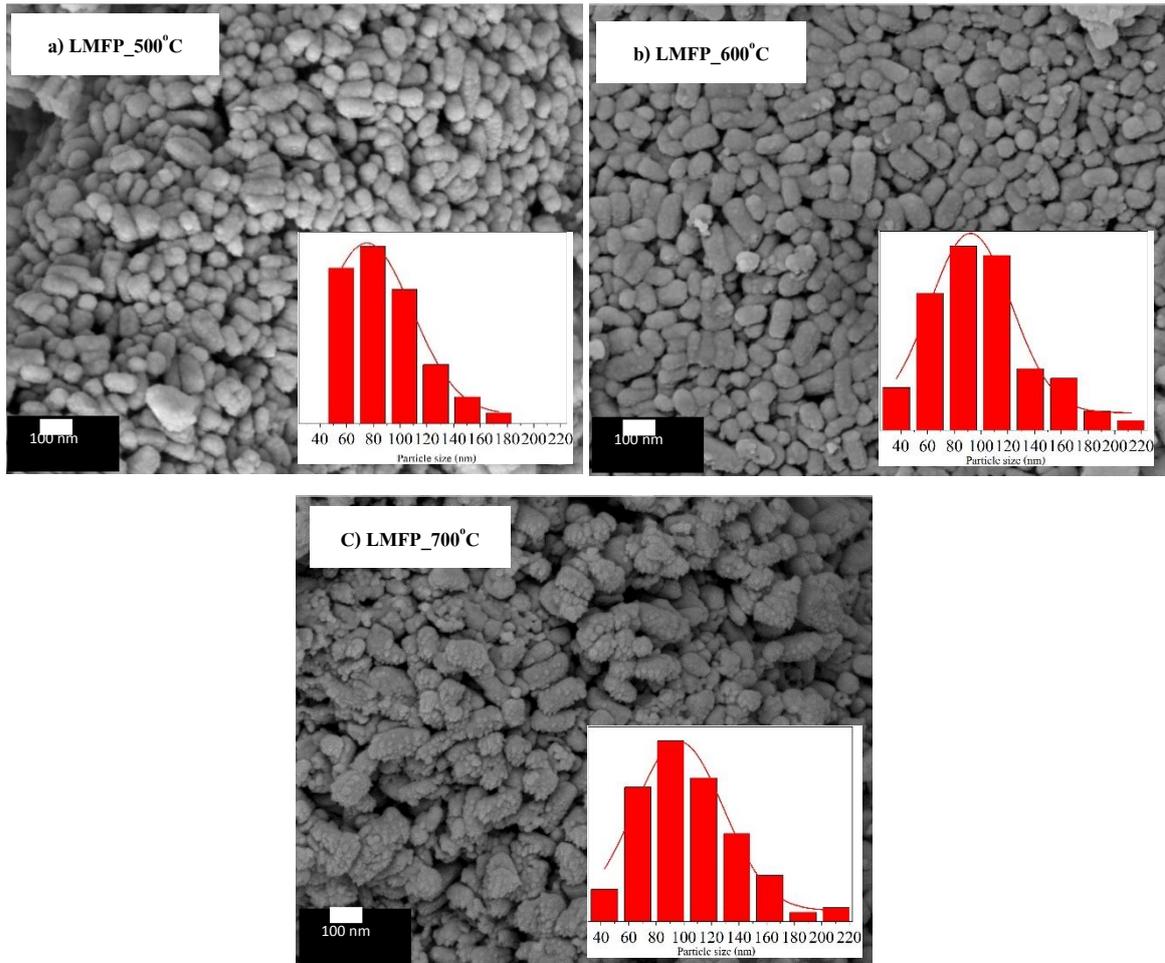


Fig. 3 Scanning electron microscopy (SEM) images of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ samples fired at (a) 500 °C (b) 600 °C and (c) 700 °C, respectively.

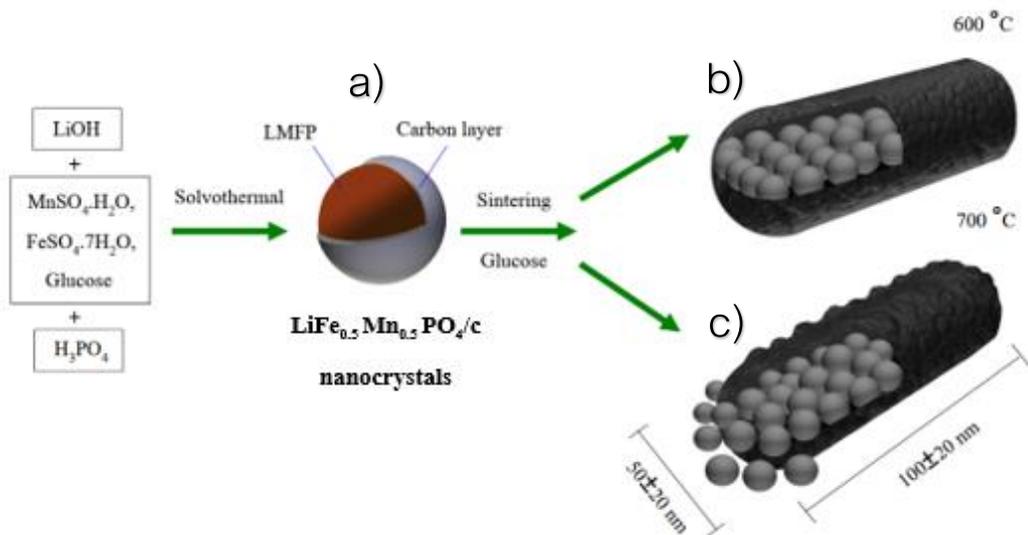


Fig. 4 Schematic of the nanocapsules consisting of carbon-coated $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ nanocrystals encapsulated by continuous carbon matrix. The nanocapsules are more uniform when fired at 600 °C, and the nanostructures are broken when fired at higher temperatures.

To further investigate the effect of firing temperature, Raman spectroscopy was employed to explore the molecular structure of the carbon phases in the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ samples (Fig. 5). The Raman spectroscopy technique is an effective method to characterize the detailed bonding structure of carbon nanomaterials. Raman spectra of carbon usually show two distinct peaks – the so called D band (due to disordered carbon features) and G band (due to the ordered graphitic carbon features). Therefore, the intensity ratio or I_D/I_G ratio represents the degree of graphitization of carbon in the reaction products (Doeff et al., 2003). As can be seen, all samples show two apparent peaks at 1350 cm^{-1} (the D band) and at 1575 cm^{-1} (the G band). The I_D/I_G ratio varied in all samples and was equal to 2.83, 2.51 and 2.81 for the samples fired at $500\text{ }^\circ\text{C}$, $600\text{ }^\circ\text{C}$, and $700\text{ }^\circ\text{C}$, respectively. This result means that the sample fired at $600\text{ }^\circ\text{C}$ showed the highest degree crystallinity of carbon in the graphite form, which can enhance the electronic conductivity of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ materials. This is consistent with previously reported results (Dhaybi et al., 2018).

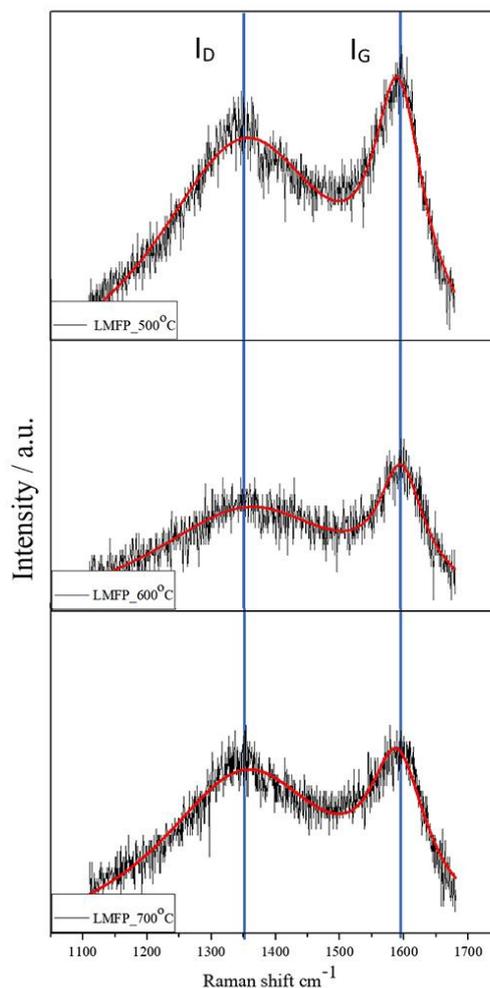


Fig. 5 Raman spectra of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ samples fired at (a) $500\text{ }^\circ\text{C}$, (b) $600\text{ }^\circ\text{C}$, (c) $700\text{ }^\circ\text{C}$.

Electrochemical properties

Fig. 6 shows the charge/discharge profiles of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ samples fired at 500 °C, 600 °C and 700 °C using an operating voltage window of 2.2 – 4.6 V at a C/10 rate. All samples show two plateau features at about 3.5 V and 4.1 V representing the redox reactions of $\text{Fe}^{2+/3+}$ and $\text{Mn}^{2+/3+}$, respectively. This result indicates that all of the synthesized $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ samples with capsule-like nanostructures exhibited excellent electrochemical performance. It is notable that these samples contained only about 5 to 10 wt% of carbon, which is much lower than 20 wt.% carbon commonly used in previous work (Kosava et al, 2018).

Additionally, the samples fired at 500 °C, 600 °C and 700 °C delivered discharge capacities of 146, 154 and 140 mAh g^{-1} , respectively. The sample fired at 700 °C showed the lowest discharge capacity while the samples fired at 600 °C gave the highest discharge capacity. This result is consistent with SEM images showing that the sample fired at 600 °C presents the most uniform and homogeneous distribution of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ nanocrystals in a carbon matrix, while the sample fired at 700 °C shows broken particles with non-uniform morphology. The sample fired at 600 °C also shows the highest degree of graphitization as indicated by the Raman spectroscopic study, which should contribute to its highest electrical conductivity resulting in the greatest discharge capacity. This means that use of the capsule-like nanostructures synthesized in this work is an effective strategy to improve the electrochemical performance of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ materials.

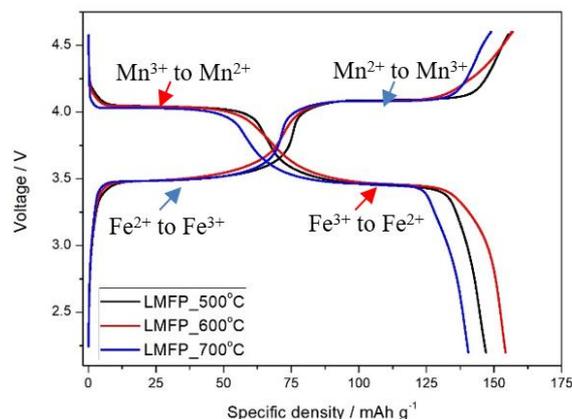


Fig. 6 Charge/discharge profiles of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ samples at C/10 rate.

Conclusions

$\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ powders can be synthesized by a solvothermal method. The materials show capsule-like morphology consisting of nanocrystals of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ homogeneously distributed in a conductive carbon matrix. Firing temperature influences the morphology and well as the degree of graphitization of the carbon phases resulting in different electrochemical performance. A discharge capacity of as high as 154 mAh.g^{-1} at a C/10 rate with only 5-10 wt.% of added carbon addition can be obtained from a $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ sample with this distinctive morphology. This means that use of the capsule-like nanostructures synthesized in this work is an effective strategy to improve the electrochemical performance of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ materials.

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