Synthesis of LiV$_3$O$_8$ Materials using Oxalic Acid as Chelating Agent

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Abstract. LiV$_3$O$_8$ was synthesised via the sol-gel method using oxalic acid as the chelating agent. Synthesis was carried out at different calcination temperatures (400 °C, 500 °C and before calcination). The structural analysis determined that the monoclinic structure of pure LiV$_3$O$_8$ formed better at a calcination temperature of 500 °C. Morphological analysis demonstrated the existence of the LiV$_3$O$_8$ rod structure.

1. Introduction

Lithium vanadate oxide (LiV$_3$O$_8$) has drawn considerable attention for use as electrode material, and offers great promise for increasing the energy density of aqueous lithium-ion batteries (LIBs) [1]. The LiV$_3$O$_8$ material is beneficial due to its high capacity, easy preparation and excellent stability in air [2, 3]. The synthesising method plays an important role in producing the best quality LiV$_3$O$_8$ materials, and can be produced by various synthesising methods for application in aqueous LIBs [4, 5].

Sol-gel is one of the best synthesis methods to produce electrode materials. The sol–gel process is a relatively easy and economical way to produce uniform particle distribution which exhibits homogeneous mixing, better crystallinity, and smaller particle size for high quality stoichiometric targeted products [6, 7]. Because LiV$_3$O$_8$ is limited by its poor electronic conductivity, oxalic acid has been added as chelating agent to produce a layer of carbon on the LiV$_3$O$_8$ rod [8]. The function of the carbon layer is to increase the electronic conductivity of LiV$_3$O$_8$. According to other reports, adjusting the quantity of the oxalic acid in the solution can control the morphology and rod size of the powder by preventing agglomeration [2, 9]. At the same time, the calcination temperature also contributes to the effect on the size [4], distribution [4] and morphology [4, 10] of the LiV$_3$O$_8$.

This work aims to study the effect of oxalic acid as chelating agent on pure LiV$_3$O$_8$. Several important material characterisations were examined to investigate the quality of the synthesised LiV$_3$O$_8$. Structural and morphological analyses are required to determine the synthesis of LiV$_3$O$_8$. 
2. Experimental study

Lithium vanadate oxide (LiV$_3$O$_8$) was synthesised by the sol-gel method. The molar ratio of lithium hydroxide mono-hydrate (LiOH.H$_2$O) (≥98.0 %, Sigma Aldrich), ammonium vanadate (NH$_4$VO$_3$) (99 %, Sigma Aldrich) and saturated oxalic acid (C$_2$H$_2$O$_4$) (≥99 %, Sigma Aldrich) in the precursor was 1:3:4. The oxalic acid was added as chelating agent, until the colour of mixture changed from buff to brown. After stirring continually at 80°C, a homogeneous dark blue was obtained. To obtain the LiV$_3$O$_8$ sample, the gel was placed in an oven to dry at 120°C and then calcined in air atmosphere by using a tube furnace at 500°C for 5 hours. The phase identification and structural analysis were carried out by (XRD, Bruker Advanced X-ray Solutions D8) in the 2θ range of 10° to 80° with monochromatised Cu Kα radiation (λ = 1.5406 Å). A Rietveld refinement was performed on the XRD data by using the Pan Analytical X’pert High Score Plus software to obtain the parameters of the structure. The morphology of the LiV$_3$O$_8$ was observed directly by field emission scanning electron microscope (FESEM, Zeiss Supra™, 35VP).

3. Results and discussion

3.1 Structural analysis

The structural analysis was examined by XRD diffraction patterns at different calcination temperatures to determine the phase of the synthesised LiV$_3$O$_8$ (Figure 1a). Before calcination, an amorphous phase demonstrated that there was no significant change. At 400°C calcination temperature, broad peaks were formed and only a few peaks occurred. By comparing this sample with the sample calcined at 500°C, all reflection peaks of LiV$_3$O$_8$ were formed. The main diffraction peaks of (100) and (111) were used to calculate the crystallite size using the Scherrer equation. The Bragg reflection peak of LiV$_3$O$_8$ was investigated in the crystalline state, and indexed to (ICDD: 98-000-4678). A monoclinic system with P2$_1$/m space group was obtained.

This result in the amorphous phase indicated that no LiV$_3$O$_8$ existed. The different calcination temperature results at 400°C and 500°C demonstrated that different phases occurred between these two calcination temperatures. Several peaks were formed at 400°C, whereas all reflection peaks were formed at 500°C. This result proved that lithium vanadate was successfully synthesised at the 500°C calcination temperature and readily oxidised to LiV$_3$O$_8$ in the crystalline phase.

The quantitative XRD analysis (Rietveld refinement method) was carried out to confirm the refined structural parameters and matching between the diffracted and reference patterns of the LiV$_3$O$_8$ (Figure 1b, 1c). During the refinement process, goodness of fit (GOF) starts out large when the model is poor, and decreases as the model produces better agreement with the data. After the simultaneous refinement of all the appropriate parameters, a visual fit of the data was obtained [11]. Numerous residual (R) values such as the weighted R profile ($R_{wp}$) and expected R ($R_{exp}$) values can be generated from the refinement process. However, the main value always defaults to $R_{wp}$ [12]. At 400°C, the visual fit of the data was not good, as the peaks did not match each other. The quality indicators were established at: GOF (9.87 %), $R_{wp}$ (19.23 %) and $R_p$ (6.42 %). However, after simultaneous refinement of all appropriate parameters at 500°C, the visual fit of the data was good, as were the quality indicators: GOF (5.44 %), $R_{wp}$ (14.04 %) and $R_p$ (6.53 %). The value is smaller than the 400°C sample. The refinement parameters are listed in Table 1.

The structural results indicated that the LiV$_3$O$_8$ synthesised at the 500°C calcination temperature was the purer sample. It achieved an ordered layered monoclinic crystalline structure with high crystallinity and a good degree of refinement. The lattice parameters of the LiV$_3$O$_8$ synthesised at 500°C calcination temperature (a = 6.644 Å, b = 3.599 Å and c = 11.809 Å) were also in good agreement.
Figure 1. XRD pattern of (a) LiV$_3$O$_8$ at different calcination temperatures, (b) observed, calculated and difference profiles from refinement of LiV$_3$O$_8$ at 400 °C and (c) 500 °C.
Table 1. Rietveld refinement parameter of the LiV₃O₈ synthesised at different calcination temperature which possesses a monoclinic crystalline structure and belongs to the P2₁/m space group.

| Parameter | 400 °C | 500 °C | (ICDD: 98-000-4678) |
|-----------|--------|--------|---------------------|
| a (Å)     | 6.65308| 6.64378| 6.6800              |
| b (Å)     | 3.59539| 3.59862| 3.600               |
| c (Å)     | 11.80681| 11.80927| 11.8377             |
| R_p (%)   | 6.41784| 6.53915| -                   |
| R_wp (%)  | 19.23263| 14.04188| -                   |
| GOF (χ²)  | 9.86976| 5.43557| -                   |
| α (°)     | 90.000| 90.000| 90.000              |
| β (°)     | 104.63090| 104.49480| 104.66300          |
| γ (°)     | 90.000| 90.000| 90.000              |
| Crystallite size (nm) | 59.61| 48.21| -                   |
3.2 Morphological analysis

The morphological analysis was executed by FESEM. The morphologies of the samples before calcination, after calcination at 400 °C, and after calcination at 500 °C were investigated at magnification (10000x) (Figure 2). Undefined shapes and sizes were observed before calcination (Figure 2a). The sample that was calcined at 400 °C demonstrated the beginnings of the rod shape formation with thin rod shapes forming (Figure 2b). The rod shape was clearly observed in the sample that was calcined at 500 °C (Figure 2c).

Based on the morphological result, the sample examined before a calcination process demonstrated undefined shapes due to the lack of heat treatment [13]. Several thin rod structures began to grow at 400 °C after the heat treatment was applied. However, these rods were not clearly defined because the applied calcination temperature was still low. The rod structure was successfully produced at 500 °C, due to the suitable selection of calcination temperature. The distributions of the rods’ size demonstrated uniform growth with an approximate diameter of about 590 nm. Hence, 500 °C is chosen as the better calcination temperature.

Figure 2. SEM micrograph at different calcination temperature of LiV$_3$O$_8$ at (a) before calcination (b) 400 °C and (c) 500 °C.
4. Conclusion

LiV$_3$O$_8$ materials were successfully synthesised by the sol-gel method using oxalic acid as chelating agent. Based on a structural analysis, the LiV$_3$O$_8$ formed a monoclinic structure due to the use of oxalic acid. The result indicated that pure LiV$_3$O$_8$ was obtained at 500 °C calcination temperature. The morphological analysis demonstrated the uniformly grown distribution of rod shapes formed at 500 °C. Hence, 500 °C was chosen as the better calcination temperature compared with 400 °C for LiV$_3$O$_8$ materials using oxalic acid as chelating agent.

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