Synthesis and characterization of high-quality cobalt vanadate crystals and their applications in lithium-ion batteries

Md. Tofajjol Hossen Bhuiyan1, Md. Afjalur Rahman1, Md. Atikur Rahman1, Rajia Sultana2, Md. Rakib Mostafa3, Asmaul Husna Tania1 and Md. Abdur Razzaque Sarker3*

Abstract: High-quality cobalt vanadate crystals have been synthesized by solid-state reaction route. Structure and morphology of the synthesized powders were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectroscopy. The XRD patterns revealed that the as prepared materials are of high crystallinity and high quality. The SEM images showed that the crystalline CoV2O6 material is very uniform and well separated, with particle size ~25 μm. The electronic and optical properties were investigated by impedance analyzer and UV–visible spectrophotometer. Temperature-dependent electrical resistivity was measured using four-probe technique. The crystalline CoV2O6 material is a semiconductor and its activation energy is 0.05 eV.

Subjects: Physical Sciences; Material Science; Physics

Keywords: CoV2O6; anode material; Li-ion battery; crystalline oxide; electrical conductivity; impedance spectroscopy

1. Introduction

Recently, lithium-ion rechargeable batteries (LIBs) have been much studied for their superior performance including high power and energy density, long life cycle, and safety. Nowadays, LIBs have wide applications in portable electronic devices such as cell phones, laptop computers, digital cameras, electronic vehicles, and power tools (Goodenough & Kim, 2010; Myung, Amine, & Sun, 2010; Song, Lee, Kim, Nazar, & Cho, 2010; Song, Lee, Kim, Nazar, & Cho, 2010; Tarascon & Armand, 2001; Yoshino, 2012). A rechargeable LIB is basically composed of an anode, a cathode, and an electrolyte. Typically, graphite is used as anode of commercial LIBs (Fan & Chen, 2011; Li, Wang, Chen, & Huang, 2009). However, graphite anode...
materials cannot meet the need of large-scale batteries in the future because of their some demer-
its such as low voltage, low capacity, and poor cyclability (Jiang, Li, Liu, & Huang, 2011). To overcome
the problem, considerable efforts should be devoted to find out alternative anode materials to re-
place graphite anode. Therefore, materials for cathodes in rechargeable LIBs have known a renewed
research interest both from the experimental and theoretical point of view (Catti, 2000; Koksbang,
Barker, Shi, & Saidi, 1996; Thackeray, 1995).

At present, transition metal vanadium-based oxides have attracted extensive attractions as an-
ode materials of LIBs for their special chemical properties. They have also applications in the fields
such as catalysts, chemical sensors, optical devices, and super capacitors for their extraordinary
physical and chemical properties (Ma, Zhang, Ji, Tao, & Chen, 2008; Mai et al., 2010; Ramkumar &
Minakshi, 2015; Shi, Li, Kou, Ye, & Zou, 2011; Xu, Lin, Jia, & Zhao, 2008). Among this group, cobalt-
based vanadate is one of the most promising materials for anode of LIBs because of its favora-
ble features such as good capacity, high discharge voltage, excellent electrochemical stability, and
life cycle (Khatun, Gafur, Ali, Islam, & Sarker, 2014). The good performance of these materials de-
deps on the properties such as grain size, quality, and perfection. The properties of cobalt vanadate
(CoV₂O₆) are governed by the condition of synthesis and subsequent processes.

The various efforts have been devoted to develop new approaches for the synthesis of CoV₂O₆
microstructures such as hydrothermal growth, sol–gel, co-precipitation, and solid-state synthesis
methods. However, these processes except solid-state reaction route require different conditions or
large quantity of solvent and organic materials (Dong, Kumada, Yonesaki, Takei, & Kinomura, 2011).
In this work, CoV₂O₆ of high quality as anode materials with high quality and crystallinity have been
prepared by solid-state reaction technique.

In this study, we devoted the efforts to prepare good quality crystalline CoV₂O₆ materials for use
as anode in LIBs with high performance. The efficiency of this material as anode depends on the
crystallinity, dislocation density, and micro-strain. The performance of this anode material also de-
deps on the activation energy and electrical and ionic conductivity at ambient and high tempera-
ture. The purpose of this work is to investigate the temperature dependence of resistivity, activation
energy, frequency dependence of impedance, charge capacity, photon wavelength dependence of
absorption of the prepared crystalline CoV₂O₆ materials. The electrochemical study of this material
is our next step. This study might play an important role to realize crystalline CoV₂O₆ as high-efficien-
cy anode material.

2. Experimental

High-purity (99.99%) powders of Co₃O₄ and V₂O₅ were used as the starting material for preparation
of CoV₂O₆. Initially, we studied the phase formation employing a thermobalance (TG/DTA 630) in
order to establish the procedure for synthesizing CoV₂O₆. A stoichiometric mixture of Co₃O₄ and V₂O₅
was heated in an air atmosphere with a heating program as shown in the inset of Figure 1. A
representative thermogravimetric (TG) curve obtained for the raw material mixture is shown in Figure 1. From this TG analysis, it was found that the weight loss at 50–600°C is too large. This suggests that at temperature lower than 50°C, the chemical reaction between the raw materials may not be active yet and there is no weight change above 700°C where the phase formation is completed.

At the first step of synthesis, the reactants were dried in air in an oven at 100°C for 12 h. A stoichiometric mixture of Co$_3$O$_4$ and V$_2$O$_5$ was mixed well in an agate mortar using ethanol, then dried and calcined at 700°C for 24 h in an air atmosphere. Before next heat treatment, the powder was grinded thoroughly to ensure homogeneity. The powder was calcined again second time at 750°C for 12 h in an air atmosphere. After second heat treatment, the powder was grinded and pelletized in 12 mm diameter under pressure of 80 Kilonewton using the pressure gauze. The compressed pellets were sintered at 850°C for 12 h under an air atmosphere. In the all heat treatments, the temperature rising and cooling rates were 3°C/min.

The powder samples were analyzed by X-ray diffraction (XRD) using a CuK$_\alpha$ ($\lambda = 0.154$ nm) radiation source using a Rigaku HYGD Multiflex X-ray diffractometer at room temperature in the center for crystal science and technology, Japan. The diffraction angle ($2\theta$) range between 5° and 85° was scanned. The morphologies and sizes of the prepared crystalline products were characterized by scanning electron microscopy (SEM). The Fourier transform infrared spectroscopy (FT-IR) spectrums were obtained within the range 200–4,000 cm$^{-1}$ region on a spectrophotometer (Spectrum 100, Perkin Elmer) using KBr as binders. Resistivity measurements were carried out by the conventional four probe method. Fine polishing was done for the disc-like samples. The Agilent Precision Impedance Analyzer (Agilent technologies, Model 4294A Japan) was used for measurements of frequency-dependent ac conductance, impedance, dielectric constant, capacitance and inductance. The samples were characterized by UV–visible spectrophotometer (Shimizu UV–1,650 PC) for wavelength-dependent absorption spectrum.

3. Results and discussion

3.1. Structural properties

Crystalline CoV$_2$O$_6$ powder was obtained by conventional solid-state reaction technique with a final firing at 850°C. The prepared CoV$_2$O$_6$ crystalline powders were characterized at the room temperature by a Rigaku Multiflex diffractometer range from $2\theta = 5$–85° with CuK$_\alpha$ radiation ($\lambda = 1.5418$Å) at 40 kV and 30 mA. The unit cell refinement was accomplished by CellCal software using XRD data as input. Typical XRD patterns of CoV$_2$O$_6$ crystalline powder shown in Figure 2 reveals that the material is single phase with monoclinic crystal structure of space group C2/m. The prepared samples were identified as highly crystalline and homogeneous by indexing these XRD patterns using JCPDS data No. 38–0090. No peaks of other phases have been detected, indicating high purity of the material. The sharp peaks indicate the good crystallinity which shows that high-quality CoV$_2$O$_6$ crystals can be...
synthesized fast by conventional solid-state reaction route. The good crystallinity of CoV$_2$O$_6$ crystals would improve the rate capability of Li-ion cells (Minakshi, Singh, Appadoo, & Martin, 2011).

In the XRD patterns, (201) peak indicates the property of brannerite-type structure of CoV$_2$O$_6$, (021) peaks indicate the property of basic unit of V–O–V bond, and the intensity ratio of (201)/(021) peaks indicates the perfection of crystallization (Guo-rong et al., 2004). The larger value of intensity ratio demonstrates the better crystallinity (Liu et al., 2002). The lattice parameters obtained from indexing of XRD pattern using CellCal program as follows: $a = 7.76\,\text{Å}$, $b = 7.41\,\text{Å}$, $c = 6.78\,\text{Å}$, $\beta = 110.62$, and $V = 365.049\,\text{Å}^3$. The calculated lattice parameters are approximately equal to the standard lattice constants obtained from the stated JCPDS data. The anion ordering in the crystal structure of anode material is one of the most important factors for good performance that is measured by the intensity ratio of the main peaks in the XRD patterns. Here, the intensity ratio of the highest peaks and second largest peak is 2.69 that are the largest among the reported results. This value represents the highest degree of anion ordering in the crystal structure of prepared cobalt vanadate. It has been proposed that the electrochemical performance of CoV$_2$O$_6$ anode material is remarkably improved when the intensity ratio of (201)/(021) peaks is higher than 1.2 (Hao, Lai, Xu, Liu, & Ji, 2005). In the XRD pattern (−201)−(200) and (110)−(210) peak doublets are well defined and separated. This suggests a dimensionally stable structure with a highly ordered distribution of anions in the lattice.

The performance of the lithium ion battery is affected by a numerous factors such as anode and cathode particle size ($D$), microstrain ($\varepsilon$), and dislocation density ($\delta$) (Yilmaz, Aydin, Turgut, Dilber, & Ertugrul, 2012). The average grain size ($D$) and microstrain ($\varepsilon$) of the CoV$_2$O$_6$ crystalline particles were calculated using Scherrer formulae, Yilmaz, Turgut, Aydin, and Ertugrul (2012) and (Rajasekar, Kungumadevi, Subbarayan, and Sathyamoorthy (2008), respectively, where $\lambda$ is the X-ray wavelength (1.5418Å), $0.94$ is the crystal shape constant, $\theta$ is the reflection angle for the highest peak, and $\beta$ is the full width at half maximum (FWHM) of the highest peak in radians. The dislocation density ($\delta$) of the crystalline CoV$_2$O$_6$ was obtained using the equation $\delta = 1/D^2$ (lines/m$^2$) (Ravichandran, Muruganatham, & Sakthivel, 2009). The calculated values are dislocation density $\delta = 8.206 \times 10^{14}$ lines/m$^2$, microstrain $\varepsilon = 1.3 \times 10^{-3}$ lines.m$^{-4}$ and average particle size $D = 110.4$ nm.

The dislocation density ($\delta$) indicates the length of dislocation lines per unit volume and measures the amount of defects in a crystal. The microstrain ($\varepsilon$) indicates strain induced in the crystalline materials that also measures the amount of defects. Here, the microstrain is very low and it means the quality of prepared CoV$_2$O$_6$ crystal was very high. The average grain size of the crystalline material is the most important factor for its applications. Here, calculated average grain size of the prepared crystalline CoV$_2$O$_6$ is 110.4 nm that is very large and hence this crystal is suitable for use as anode material in the high-efficiency Li-ion batteries.

In order to get physical insights of the chemical bonding and phase formation, we also studied the structure by FT-IR spectroscopy. FT-IR spectroscopic technique is powerful for investigating the local structure and cation environment in oxides (Amdouni, 2003; Julien, 2000). The spectroscopic spectrum of crystalline CoV$_2$O$_6$ is shown in the Figure 3 that contains the main absorption bands at: 279, 390, 528, 847, 1,010, 1,103, 1,385, 1,638, 3,411, 3,806, 3,853, and 3,951 cm$^{-1}$. These results confirm the XRD observations showing that the vibration bands for precursors vanished and the vibration bands for the oxide network developed.

In the far-infrared region, we observed the single well-resolved band at 279 cm$^{-1}$. This sharp band in CoV$_2$O$_6$ is assigned due to an asymmetric stretching motion of the CoO$_6$ octahedron that is highly distorted (Kim et al., 2012). It is the unique fingerprint of the Co site occupancy in the monoclinic structure of CoV$_2$O$_6$ crystal. The absorption band at 847 and 552 cm$^{-1}$ can be attributed to the symmetric and asymmetric stretching of VO$_5$ units, respectively (Tang, Zhou, Liu, Liu, & Liang, 2013). The absorption bands at 854 cm$^{-1}$ of CoV$_2$O$_6$ may be assigned to V = O stretching mode (Song et al., 2009). The absorption bands in the region of 500–700 cm$^{-1}$ are due to the V–O–V bonds
corresponding to the asymmetric or symmetric stretches (Gao, Ruiz, Xin, Guo, & Delmon, 1994) and the bands at 386 cm⁻¹ can be assigned to the stretching of Co–O modes. There is a sharp medium absorption peaks around 1,104 cm⁻¹, which is due to the vibrations of the cobalt vanadate crystal lattice. The results of FT-IR analysis were good agreement with XRD results.

The morphologies of the as-prepared CoV₂O₆ crystalline materials were examined by SEM. Figure 4 shows the typical SEM micrographs of the CoV₂O₆ crystalline materials with different magnifications. The SEM images reveal that the CoV₂O₆ crystals consists of large grain size of about 2–10 μm, mixed with some small particles of sizes about 500 nm. The SEM images also reveal that the particles are very uniform and their surfaces are smooth. The particles are well separated from each other. Therefore, ample space between the particles can be clearly observed. The prepared CoV₂O₆ material
with highly crystalline large size particles was expected to have better electrochemical performances.

3.2. Electronic properties

The temperature-dependent dc resistivity of the samples was measured using four probe techniques from room temperature to 500 K as shown in Figure 5. The obtained results reveal that the resistivity of crystalline CoV₂O₆ decrease with temperature and it was signature of the semiconducting behavior. At ambient pressure, ρ(T) of crystalline CoV₂O₆ materials exhibits semiconducting-like behavior in which dρ/dT < 0 over the entire range of temperature. The variation of ln of conductivity (lnσ) with inverse temperature (K⁻¹) for CoV₂O₆ crystals have been shown in Figure 6. The activation energy can be obtained using Arrhenius relation

\[ \sigma = \sigma_0 \exp\left(-\delta E/2K_B T\right) \]

where \( \delta E \) is the activation energy, \( K_B \) in the Boltzmann constant, and \( \sigma_0 \) is the pre-exponential factor. From slope of the \( \ln\sigma \) vs. \( K^{-1} \) plot, the activation energy was calculated at low- and high-temperature region (Sivaprakash, Majumder, Nieto, & Katiyar, 2007). The activation energy \( \delta E = 0.15 \) eV is higher than that of \( \delta E = 0.013 \) The higher values indicate that conductivity is associated with the free band transition of carriers, i.e. transition from donor level to conduction band and the low values of \( \delta E \) may be associated with the localized levels hopping due to the excitation of carriers from one defect state to another.

The frequency-dependant impedent was measured by impedance analyzer, frequency was varied from 100 Hz to 10 MHz and oscillatory voltage was 300 mV. Figure 7(a) shows the frequency-dependent impedance of CoV₂O₆ crystals. Figure shows two regions, high-frequency and low-frequency regions. At high frequencies, the real part of the impedance is almost independent of the frequency, which is attributed to the resistance effect. In the low-frequency regions, impedance considerably decreases as the frequency increases. This indicates that the components of capacitance and resistance of the equivalent element is active in this region.
Figure 7. Frequency-dependent (a) impedance, (b) capacitance, (c) dielectric constant (d), and magnetic induction of the CoV$_2$O$_6$ sample.

Figure 8. The UV–visible absorption spectrum of the CoV$_2$O$_6$ sample.
The capacitance and dielectric properties of the samples were measured by precision impedance analyzer at the same condition as impedance measurement. Silver paste was coated on both surface of the sample before measurement. Dielectric constant is a measure of materials ability to store electric charge. The frequency-dependent capacitance of samples measured at room temperature is shown in Figure 7(b). The capacitance of CoV₂O₆ crystal is high at low-frequency region due to contribution of all kinds of polarization at low frequency, then decreases with increase of frequency and finally approaches to all most constant value above 8 MHz. This is due to the change of space charge, ionic and orientation polarization at higher frequencies (Kingegy, 1960). Figure 7(c) shows the frequency-dependent dielectric constant of the CoV₂O₆ crystals that implies the same tendency of capacitance. Figure 7(d) shows the frequency-dependent magnetic induction of the CoV₂O₆ crystals at the room temperature. Initially, the magnetic induction increases with frequency and then decreases. This plot shows that the sample was free of magnetic impurities.

3.3. Optical properties

The optical properties of a material are very important in some applications such as optical coatings, reflectors, absorbers, and various optoelectronic devices. The reported results on optical absorption or transmission of CoV₂O₆ crystals are not available. In this study, UV–visible absorption spectrum of the CoV₂O₆ crystals was recorded using a UV–visible spectrophotometer (Shimazu: UV-1650 PC) in the photon wavelength range 200–800 nm. Figure 8 shows the absorption spectrum of CoV₂O₆ crystals. The absorption slightly increases with increase of wavelength in the visible region. There are some absorption peaks in the ultraviolet region. There are two very strong absorption peaks at 200 and 206 nm and a medium peak at 209 nm. These peaks reveal the absorption criteria of cobalt vanadate in the ultraviolet–visible region.

4. Conclusions

In this study, cobalt vanadate (CoV₂O₆) crystalline materials of high crystallinity and high purity have been successfully prepared by solid-state reaction technique. This technique is most effective to grow high-quality crystalline material at required high temperature. The CoV₂O₆ poly crystals were obtained after two times calcinations at 700 and 750°C. Dense crystalline pellets were obtained by sintering at 750°C and its structural, electrical, and optical properties were studied. From structural properties and crystal quality studies, it has been assessed that high-quality CoV₂O₆ was successfully synthesized. We want to propose here that high-quality CoV₂O₆ crystals prepared by solid-state reaction technique may enhance the efficiency of Li-ion batteries. The charge capacity and dielectric constant of CoV₂O₆ crystal is high at room temperature but activation energy is high at above the room temperature. The CoV₂O₆ crystal might be a weak absorber at the ultraviolet region. In the next stop, we want to investigate the electrochemical properties of this material for battery applications.

Acknowledgments

Authors would like to thanks Rajshahi University, Rajshahi, Bangladesh authority for providing funds under the University Research Grant. Authors also would like to thanks Ministry of Science and Technology, Govt. of Bangladesh for providing scholarship to carry out this work.

Funding

This work was partially supported by the Rajshahi University Research (grant number A774) and University Grand Commission, Bangladesh.

Author details

Md. Tofajjol Hossen Bhuiyan1
E-mail: thbapon@pust.ac.bd
Md. Afjalur Rahman1
E-mail: afjal.sust36@gmail.com
Md. Atikur Rahman1
E-mail: atik0707phy@gmail.com
Rajia Sultana2
E-mail: sultanarajia.accedu@gmail.com
Md. Rakib Mostafa3
E-mail: rakibmostafa6@gmail.com
Asmaul Husna Tania3
E-mail: ahtania810@gmail.com
Md. Abdur Razzaque Sarker3
E-mail: razzaque.ru2000@yahoo.com
1 Department of Physics, Pabna University of Science and Technology, Pabna 6000, Bangladesh.
2 Centre for Advanced Research in Sciences (CARS), University of Dhaka, Dhaka, Bangladesh.
3 Department of Physics, University of Rajshahi, Mothihar, Rajshahi 6205, Bangladesh.

Citation information

Cite this article as: Synthesis and characterization of high-quality cobalt vanadate crystals and their applications in lithium-ion batteries, Md. Tofajjol Hossen Bhuiyan, Md. Afjalur Rahman, Md. Atikur Rahman, Rajia Sultana, Md. Rakib Mostafa, Asmaul Husna Tania & Md. Abdur Razzaque Sarker, Cogent Physics (2016), 3: 1265778.
