






Full length article

Investigation of various cobalt concentrations on LiV_2O_5 as cathode materials with tunable high rate capability and operating voltage in Li-ion batteries

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Highlights

- One pot hydrothermal method gives rod and shape morphologies enhances the electrochemical properties.
- $\text{LiCo}_{0.1}\text{V}_2\text{O}_5$ shows improve rate capability with stable and fast cycling.
- It delivered high reversible capacity with long cycle life especially at high current rates.
- Lower charge transfer contributed to the improved high rate capability with stable cycling.

Abstract

Li-ion batteries discover its way in developing new electrodes with recent advancements. In regardless, the new electrode materials necessity is to fulfill the high voltage operation with high current rate for Li-ion batteries. Hence, $\text{LiCo}_x\text{V}_2\text{O}_5$ ($x=0.1, 0.3$ and 0.5) were synthesized by one pot hydrothermal synthesis followed by post calcination. The powder X-ray diffractometer explains the formation of $\text{LiCo}_x\text{V}_2\text{O}_5$ ($x=0.1, 0.3$ and 0.5) with more than two phases as the cobalt concentration increases with increased grain size. FE-SEM and HR-TEM studies of the as-synthesized materials shows the formation of sphere and rod like morphologies. Cyclic voltammograms reveal an excellent redox peaks for Co and V, the redox peaks were observed between 2.0 and 4.5 V. $\text{LiCo}_{0.1}\text{V}_2\text{O}_5$ material delivered high reversible capacity of 147mAh/g especially at high current density as well as withstand stable discharge capacity up to 50 cycles. The charge-discharge cycling of $\text{LiCo}_{0.1}\text{V}_2\text{O}_5$ cathode materials at various rates 0.5C, 1C, 2C, 3C and 4C delivered specific discharge capacities of 147mAh/g, 129mAh/g, 113mAh/g, 98mAh/g and 85mAh/g with 96% columbic efficiency. Also it shows the lower charge transfer resistance with less interfacial properties, which contributed to the improved rate capability with stable cycling. Thus this material serves as promising cathode material for rechargeable Li-ion batteries.

Introduction

The rapid hike in the human population urges us to use increased amount of fossil fuels, which causes CO_2 emission to increase. Because of which global warming, ozone depletion and other natural disaster are occurring. To downturn the usage of fossil fuel, and to reduce the usage of non-renewable energy sources, electrochemical energy storage devices such as

capacitors [[1], [2], [3]], fuel cells [4] and rechargeable batteries [[5], [6], [7], [8], [9]] plays a major role. The rechargeable batteries nowadays gain attention because of its usage in high voltage applications such as in UPS power grid, hybrid electric vehicles (HEV), etc.

Particularly Li-ion batteries have now become mature technology because of the usage of already available active materials as electrode [10,11]. This brings out the rapid development of electrode materials out of metal oxides, metal complexes and new kinds of polyionic materials.

Polyionic materials provide a greater platform for its use as cathode due to its multiple valent ions with the various oxidation states. K. S. Nanjundaswamy et al. [12] in his work explained polyionic ions are large enough to occupy the lattice sites which in turn boost the cathode redox potential thereby enhancing the structural stability. For example, many mixed metal polyionic materials such as LiMnPO_4 [13], $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ [14], $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ [15], $\text{Li}[\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}]\text{O}_2$ [16], LiCoVO_4 [[17], [18], [19]], LiNiVO_4 [17,20] and LiV_2O_5 (LVO) [21,22] have also been developed due to its stability, high power and energy density. Among these materials LVO-type cathode material shows advantages such as higher Li ion diffusion coefficient and electronic conductivity, in $\gamma\text{-LiV}_2\text{O}_5$ puckered layered framework Li ions are located between the $(\text{VO}_5)_n$ layers which helps during the intercalation-deintercalation mechanism, and also in recent years it attained greater attention as a low-cost cathode materials for Li-ion batteries [23]. At the same time it shows some disadvantages including defects in structure during high current rate operations [24]. And also, most of the works are done with higher concentrations of cobalt [25,26]. As the cobalt metal is expensive as well as toxic, therefore the studies should focus on high voltage cathode materials at higher C-rate while reducing the cobalt concentrations.

In this work, we focus on synthesizing high rate capable cathode materials to the LiV_2O_5 by various cobalt concentrations and they were characterized by various physical characterization techniques including X-ray Diffraction (XRD), Attenuated Total Reflection-Fourier Transmission Infrared Spectroscopy (ATR-FTIR), Field Emission-Scanning Electron Microscope (FE-SEM), High Resolution-Transmission Electron Microscope (HR-TEM), followed by the electrochemical studies such as Cyclic Voltammetry (CV), Galvanostatic Charge/Discharge studies and Electrochemical Impedance Spectroscopy (EIS).

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Section snippets

Synthesis of $\text{LiCo}_x\text{V}_2\text{O}_5$ ($x = 0.1, 0.3$ and 0.5) cathode materials

Li_2CO_3 (Aldrich) were used as a source of lithium, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) as a source of cobalt, Citric acid (Aldrich) as a reducing agent as well as chelating agent [27], NH_4VO_3 (Sisco Research Laboratories) as a source of vanadium. The chemicals with purity were received and used in experiments without further purification. The $\text{LiCo}_x\text{V}_2\text{O}_5$ ($x = 0.1, 0.3$ and 0.5) materials were synthesized by hydrothermal synthesis followed by calcination. Stoichiometric amount of NH_4VO_3 were dissolved in 80 ml

Powder X-ray diffraction characterization (PXRD) of $\text{LiCo}_x\text{V}_2\text{O}_5$ ($x = 0.1, 0.3$ and 0.5) cathode materials

The prepared samples LCVO1, LCVO2 and LCVO3 were characterized using powder XRD and the respective spectrum were given in the Fig. 1. The major intense peaks are 20.8° , 22.1° , 23.6° , 27.5° , 32.0° , 35.3° . LCVO1 and LCVO2 almost show similar kind of diffraction pattern with the slight shift in the 2 theta values. The shift in the 2 theta values is due to the increase in the cobalt concentration, as increase the larger radii of cobalt influences the lattice expansion [28]. Out of these major

Conclusion

$\text{LiCo}_x\text{V}_2\text{O}_5$ ($x = 0.1, 0.3$ and 0.5) materials were synthesized by hydrothermal method followed by calcination at 900°C . Structural characterizations such XRD confirms the formation of secondary phases such as LiV_2O_5 and Co_3O_4 phases, other than that VO_2 resulted for the 0.5 of cobalt concentration. The average grain size from the major intense XRD peaks were calculated as 2.63 nm, 2.76 nm and 3.14 nm for LCVO1, LCVO2 and LCVO3. ATR-FTIR results confirms the formation of the desired $\text{LiCo}_x\text{V}_2\text{O}_5$

Acknowledgements

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...The diffraction pattern for Na2TP shown in Fig. 2c is well associated with the Pbc21 space group and their lattice parameters are $a = 3.558 \text{ \AA}$, $b = 10.849 \text{ \AA}$, $c = 19.109 \text{ \AA}$, $\beta = 90.0$, and cell volume $V = 737.79 \text{ \AA}^3$, also their refined data is summarized in Table S2 and the representative schematic illustration of the Na2TP crystal structure is shown in Fig. 2d. From the crystal structure, it is deduced that the Na^+ ions are occupied in tetrahedral structure and terephthalate anions resemble in the γ - packing of an aromatic compound, which is reported elsewhere [39]. The crystalline size calculated through the scherrer equation is $\sim 39 \text{ nm}$ for TPA and $\sim 61 \text{ nm}$ for Na2TP considering the high intense diffraction peak in both the material with the corresponding d-spacing values 5.124 \AA and 5.214 \AA , respectively [40]. The FT-IR spectroscopy is used to predict the functional groups of an organic compound with the help of the absorbance value....

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...With these effects commercialization of Li-ion batteries (LIBs) received much attention due to their high energy density, cyclability, and many other factors [1]. But other limitations of high cost, safety and transportation made an alternative search for Li-ion batteries [2]. Hence Sodium (Na) metal located beneath lithium (Li) in the periodic table and share similar chemical properties in plenty of factors, Na-ion batteries (NIBs) are the next complement to LIBs [3]....

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...The plot is obtained at a frequency range of 0.01 Hz–100 KHz before and after cycling for anode and cathode, respectively. It consists of two regions including semicircle/arc followed by the inclined straight in lower and higher frequency ranges ascribed to charge transfer resistance and diffusion of Li-ions [49,50]. In the case of anode material before cycling of both the H-POM and Li-POM cathode materials exhibit low charge transfer resistance rather after cycling....

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