

Synthesis and Characterization of Lithium Vanadates for Electrochemical Applications

VS Reddy Channu^{1,2,*}, Rudolf Holze¹, Edwin H. Walker Jr.², S.A. Wicker Sr², Rajamohan R. Kalluru³, Quinton L. Williams³, Wilbur Walters³

¹ Institut für Chemie, AG Elektrochemie, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

² Department of Chemistry, Southern University and A&M College, P.O. Box 12566, Baton Rouge, LA 70813

³ Department of Physics, Atmospheric Sciences and Geoscience, Jackson State University, JSU Box. 17660, 1400 J.R. Lynch Street, Jackson, MS 39217

*E-mail: chinares02@gmail.com

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Nanosized lithium vanadate materials were synthesized by controlling the pH of the lithium hydroxide solution of vanadium pentoxide using precipitation and hydrothermal methods. The crystal structure and phase purity of the samples were examined by powder XRD. The samples were identified as $\text{LiVO}_3/\text{Li}_4\text{V}_{10}\text{O}_{27}$ (pH = 2, 6 precipitation method) and LiV_3O_8 (pH = 2 and 6, hydrothermal method). The O_2 treated lithium vanadates (pH = 2 and 6, precipitation method) were identified as $\text{LiVO}_3/\text{Li}_3\text{VO}_4$. The electrochemical properties of the cathode made of lithium vanadate nanomaterials are discussed.

Keywords: Precipitation and hydrothermal synthesis, morphology, cyclic voltametry, lithium battery

1. INTRODUCTION

The development of energy storage systems, like batteries and capacitors, with reduced size, weight and cost are important for a variety of tactical and strategic applications: electric guns, electric armor, microwave sources and ballistic missile [1, 2]. Lithium ion rechargeable batteries are now widely used as the power source for mobile electronic systems such as mobile phones, camcorders, laptops and personal digital-assistants (PDAs). Presently, transition metal oxides containing Li, such as LiNiO_2 , LiMn_2O_4 and mostly LiCoO_2 , are used for cathodes in rechargeable batteries [3]. However, owing to the fact that Co is a scarce material, an alternative cathode material for LiCoO_2 is now greatly

desired. Currently, LiMn_2O_4 or Mn based oxides are the most promising alternative cathode materials [4]. However, capacity degradation at higher temperatures causes a problem when Mn based oxide cathodes are used in Li ion rechargeable batteries[5]. Therefore, we have focused on the development of alternative new cathode materials, such as lithium vanadium oxide nanomaterials, using cost-effective synthesis for improved performance of the Li ion rechargeable battery.

Lithium vanadium oxides have been investigated as a cathode material for secondary batteries because of attractive characteristics such as high specific energy, good rate capacity and good cycle stability [6]. The preparation and post-treatment steps were found to significantly influence the microstructure of the materials and the electrochemical properties of lithium vanadium oxides [7]. The traditional solid-state method was used to synthesize LiV_3O_8 by chemical reaction between Li_2CO_3 and V_2O_5 at 680 °C for 10 h [8]. To overcome the difficulties arising from solid state reactions such as maintaining composition control and homogeneity of particle size, and electrochemical performances, other techniques were used to improve the electrochemical performance of lithium vanadium oxide [9-12]. In recent times, more attention has been given towards increasing the specific capacity of lithium vanadium oxide materials [13-19]. Guo's group reported a large enhancement in electrical conductivity and strength of the electrodes prepared by lithium vanadium oxide composites, such as polypyrrole- LiV_3O_8 composite [15], and yttrium-doped LiV_3O_8 [16]. Other groups also made an efforts on the preparation of LiV_3O_8 nanostructures, such as nanosheets [20], nanobelts[18], nanorods [10], nanowires [21], and the study of their electrochemical performance. In previous work, we have paid special attention on the fabrication of electrode materials, such as V_2O_5 nanostructures [22], VO_2 (B) nanorods [23], and MoO_3 nanostructures [24, 25] by a hydrothermal route. In this work, the lithium vanadate nanostructures were synthesized using precipitation and hydrothermal methods for improving electrochemical applications.

2. EXPERIMENTAL

V_2O_5 powder (99.5%) was dissolved in 1 M $\text{LiOH}\cdot x\text{H}_2\text{O}$ solution (0.2 M) at room temperature. To investigate the influence of pH values, a set of experiments were designed with the pH of the solution being adjusted to 2 and 6 by adding 3M HNO_3 solution. A part of the pH-adjusted solution was placed in an oven for aging at 90 °C for 4 days. The clear solution turned orange and red upon aging, while its viscosity progressively increased. A dense colloid suspension with dark red color was formed. The dense colloid suspension obtained was dried at 60 °C for 48 h under static-air conditions. Leftover pH-adjusted solution was transferred to a 25-mL-Teflon lined autoclave. The autoclave was kept at 200 °C in an oven for 4 days. The final products were filtered, washed with distilled water, and dried in air. Calcination was performed at 400 °C for 6 h.

Crystallographic information of the samples was obtained using a Bruker Advanced D8 X-ray powder diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation ($\lambda=1.54187$ Å). Diffraction data were collected over the 2θ range from 5 to 70°. The morphologies of the resulting products were characterized by scanning electron microscopy (JEOL, JSM 6390).

Cyclic voltammetric (CV) properties of the lithium vanadates were investigated with a three-electrode cell with a platinum counter electrode and a silver (Ag) wire reference electrode. The working electrode, prepared by mixing 80 wt% of active material, 15 wt% of acetylene black and 5 wt% of poly (tetrafluoroethylene) (PTFE), was then coated on a 1.0 cm² ITO glass. A solution of 1 M lithium perchlorate in propylene carbonate was used as the electrolyte, after purification by recrystallization of lithium perchlorate (99.99%, Aldrich) and by distillation of propylene carbonate (99.7%, Aldrich), respectively. Cyclic voltammetric (CV) measurements were carried out between the potential limits of -1.0 V and +1.0 V versus the Ag reference electrode using a potentiostat/galvanostat (PRE 273). The CV curves were recorded at a scan rate of 5mV/s.

3. RESULTS AND DISCUSSION

The crystal structure and phase purity of the samples have been examined by powder XRD. The lithium vanadates which were prepared the using precipitation method with different molar ratios of lithium vanadium oxide solution (pH = 2) are identified as LiVO₃/Li₄V₁₀O₂₇ (Fig.1).

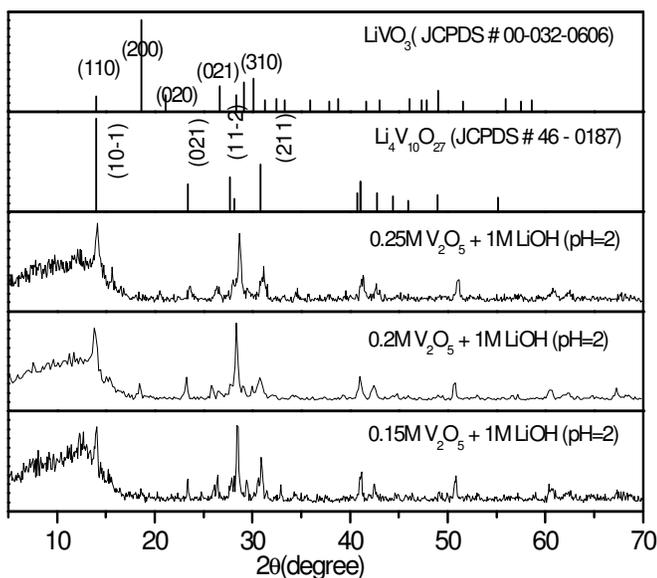


Figure 1. XRD patterns of lithium vanadates using a precipitation method.

The samples are identified as LiVO₃/Li₄V₁₀O₂₇ (pH = 2, 6 precipitation method) and all of the reflection peaks are indexed as monoclinic LiVO₃ (JCPDS No: 32-0606) and Li₄V₁₀O₂₇ (JCPDS No: 00-046-0187) with lattice parameters of a = 10.156Å, b = 8.399 Å and c = 5.885Å, β = 110.42° and a = 9.1077 Å, b = 9.46070 Å and c = 6.84260 Å, β = 111.77° (Fig.2). The O₂ treated samples prepared by the precipitation method from the solutions of pH = 2, 6 are identified as LiVO₃/Li₃VO₄. The majority

of the diffraction peaks were indexed with the monoclinic LiVO_3 (JCPDS No: 00-033-0835) with lattice parameters of $a = 10.179 \text{ \AA}$, $b = 8.425 \text{ \AA}$ and $c = 5.895 \text{ \AA}$, $\beta = 110.545^\circ$ and a few peaks were indexed with the orthorhombic Li_3VO_4 (JCPDS No: 00-039-0378) with lattice parameters of $a = 6.319 \text{ \AA}$, $b = 5.448 \text{ \AA}$ and $c = 4.94 \text{ \AA}$ (Fig. 3).

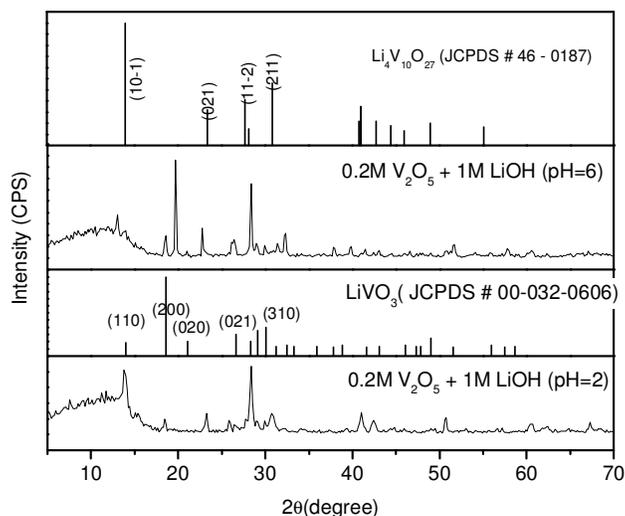


Figure 2. XRD patterns of lithium vanadates using precipitation method by various pH values of solution

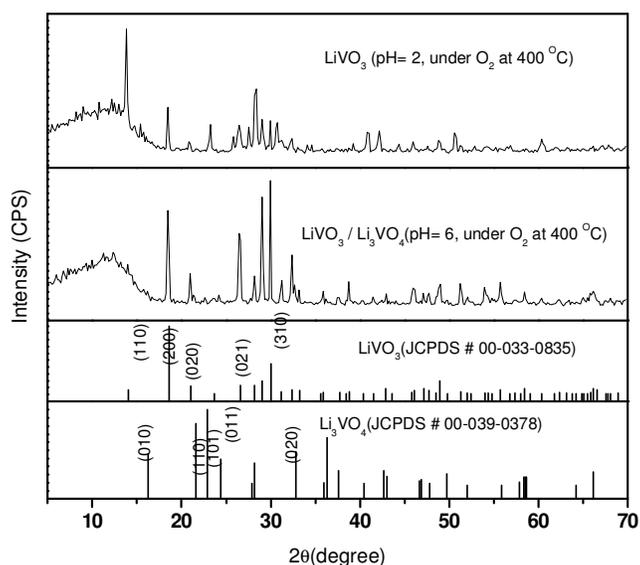


Figure 3. XRD patterns of O_2 treated lithium vanadates using precipitation method by various pH values of solution.

All the diffraction peaks of the sample prepared with the hydrothermal method from the solutions of pH = 2, 6 are indexed to monoclinic structure phase of $P21/m$ LiV_3O_8 (JCPDS No: 00-72-1193) with lattice parameters of $a = 6.68 \text{ \AA}$, $b = 3.596 \text{ \AA}$ and $c = 12.024 \text{ \AA}$ (Fig.4 and Fig.5).

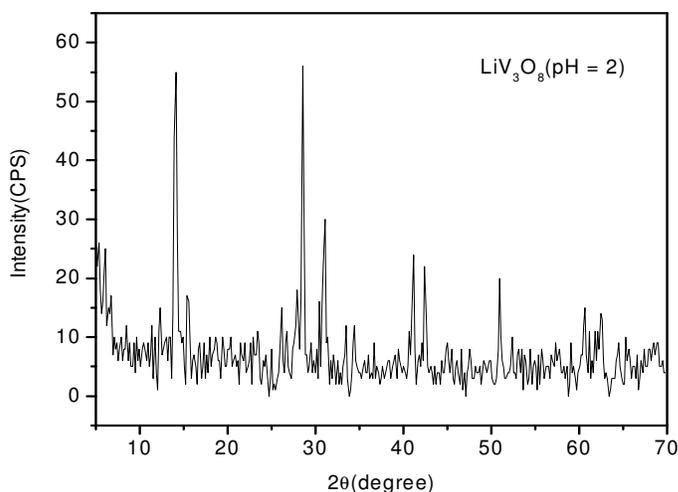


Figure 4. XRD patterns of lithium vanadates(pH = 2) using hydrothermal method .

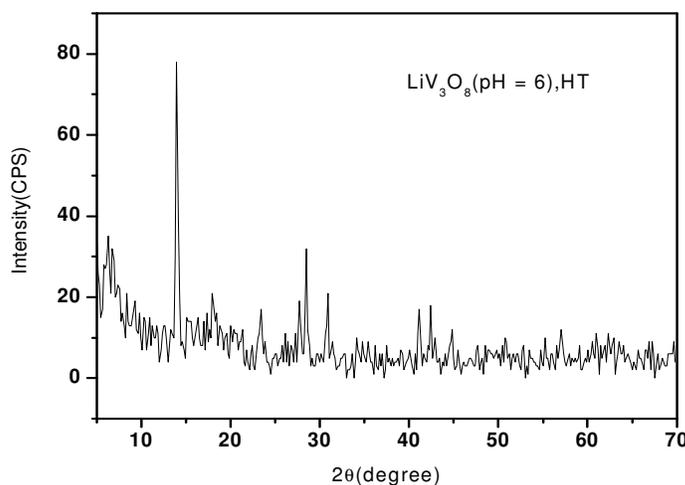


Figure 5. XRD patterns of lithium vanadates(pH = 6) using hydrothermal method.

Nanoneedles with diameters ranging from 200 to 500 nm and a thickness of 60 nm of $\text{LiVO}_3/\text{Li}_4\text{V}_{10}\text{O}_{27}$ prepared by the precipitation method (pH=2) are shown in Fig.6a. Rod-shaped lithium vanadate with the width of ca. 200 nm and several micrometers in length prepared by precipitation from the aqueous lithium vanadate solutions (pH =6) are shown in Fig.6b. LiV_3O_8 nanobelts were synthesized using the hydrothermal method from the lithium vanadate solutions (pH =

2, 6). The nanobelts are long with a typical length of 6 μm and diameter ranging from 100 to 500 nm (Fig.7a & b). The synthesized LiV_3O_8 from the pH = 6 lithium vanadate solution by hydrothermal method, grows in particular belt shape morphology with four sharp corners, compared to that of LiV_3O_8 nanobelts prepared with the pH = 6 lithium vanadate solution.

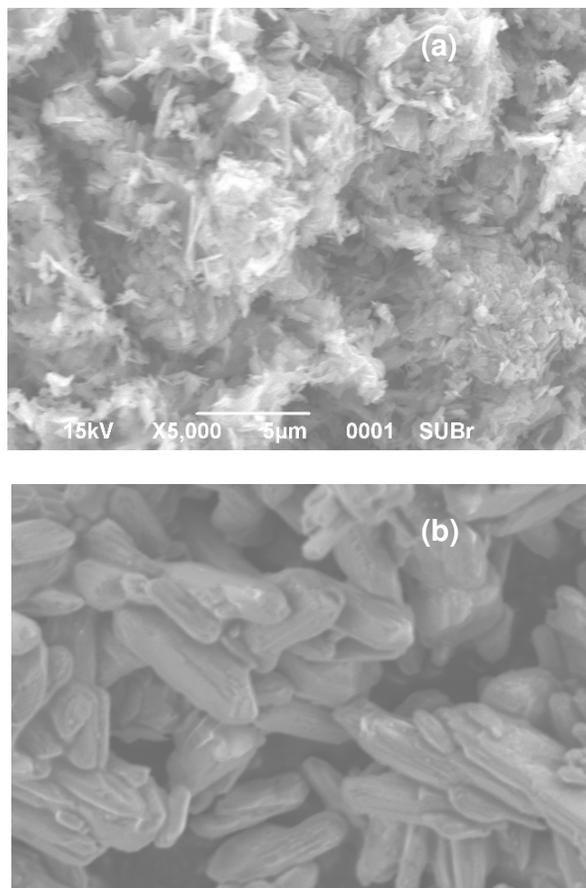


Figure 6. SEM images of lithium vanadates (pH = 2, 6) using precipitation method.

One can synthesize a large amount of lithium vanadate nanomaterials at low temperatures without a delicate equipment and sophisticated templates or catalysts through cost-effective synthetic procedures described in this article. Because the crystal structure of lithium vanadates has two dimensional layered structures, lithium vanadate nanomaterials grow as belts and rods with the directional growth along a particular axis.

The cyclic voltammograms (CVs) of the lithium vanadate nanomaterials prepared from the precipitation without O_2 -treated and O_2 -treated and the hydrothermal methods are shown in Fig. 8a–f. The CV of lithium vanadate (pH = 2, precipitation method) nanomaterials exhibit one broad anodic peak at 0.04 V and two cathodic peaks at -0.64 V and +0.31 V, respectively (Fig. 8a). The CV of a working electrode made of O_2 -treated lithium vanadate (pH = 2, precipitation method) reveals one broad anodic peak at 0.064V and two cathodic peaks at -0.63V and +0.41V, respectively (Fig. 8b). The

broad anodic peak at +0.29 V and a cathodic peak at -0.39 V were identified on the CV of lithium vanadate (pH = 6, precipitation method) (Fig.8c). The CV for a working electrode made of O₂- treated lithium vanadate (pH = 6, precipitation method) shows one broad anodic peak at +0.33 V and a cathodic peak at -0.49 V (Fig. 8d).

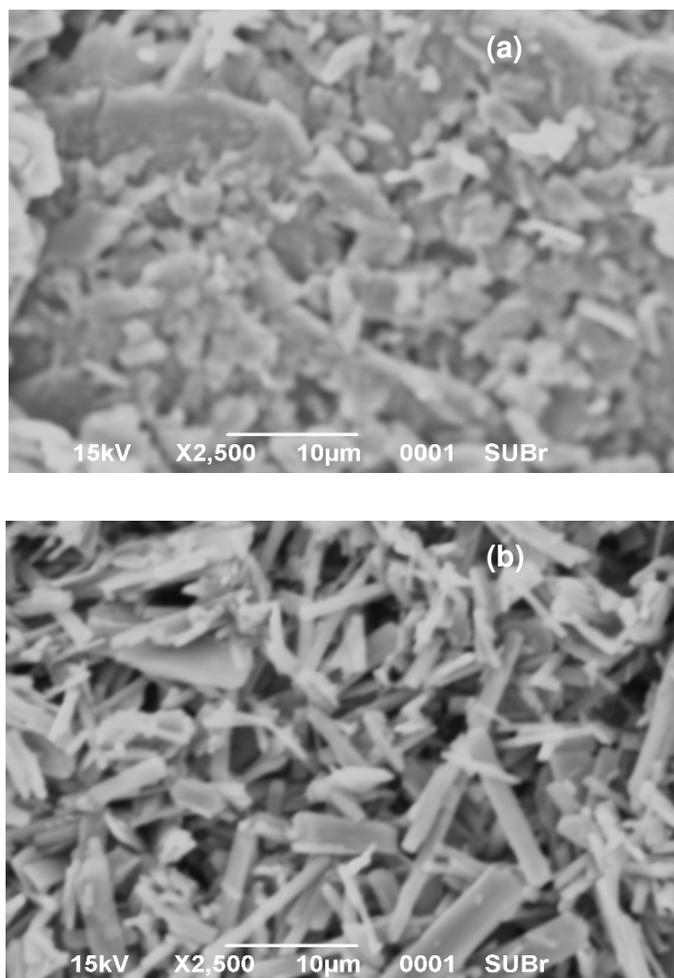


Figure 7. SEM images of lithium vanadates (pH = 2,6) nanobelts using hydrothermal method.

The CV of the working electrode made of hydrothermal synthesized lithium vanadate from pH = 2 solution exhibits one broad anodic peak at +0.035 V and one broad cathodic peak at +0.36V (Fig.8e). The CV of the hydrothermal synthesized lithium vanadate nanobelts yielded from pH = 6 solution demonstrate two anodic peaks are at -0.25 and +0.55V, and two cathodic peaks are at -0.64V and +0.32V (Fig.8f). The anodic peaks are attributed to the lithium ion leaving out and the cathodic peaks are attributed to the lithium ion inclusion from and to the working electrode materials.

The CVs of each lithium vanadate electrodes show different anodic and cathodic peak positions and also different shapes in CVs, indicating a significant difference in the electrochemical property,

caused by different morphologies of the lithium vanadate nanomaterials prepared by both precipitation and hydrothermal methods.

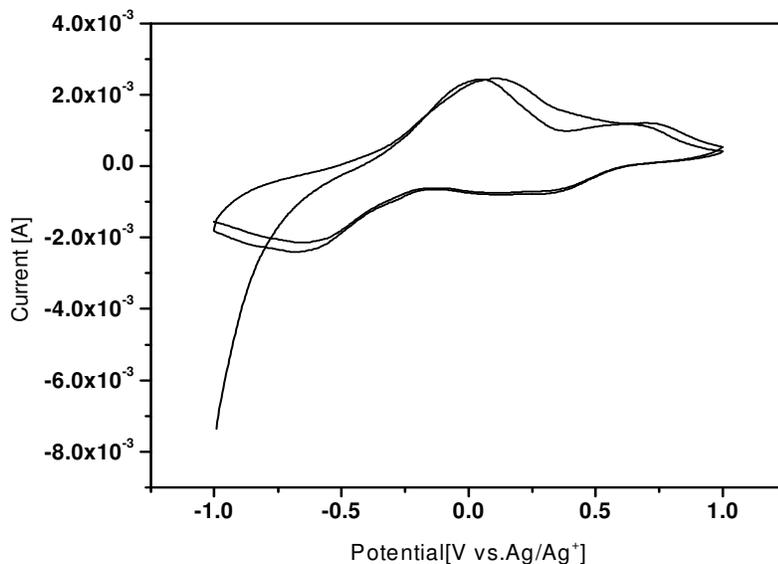


Figure 8(a). Cyclic voltammogram of lithium vanadate (pH = 2, precipitation method) in non- aqueous electrolyte (1M LiClO₄ dissolved in propylene carbonate) with scan rate 5mV/s.

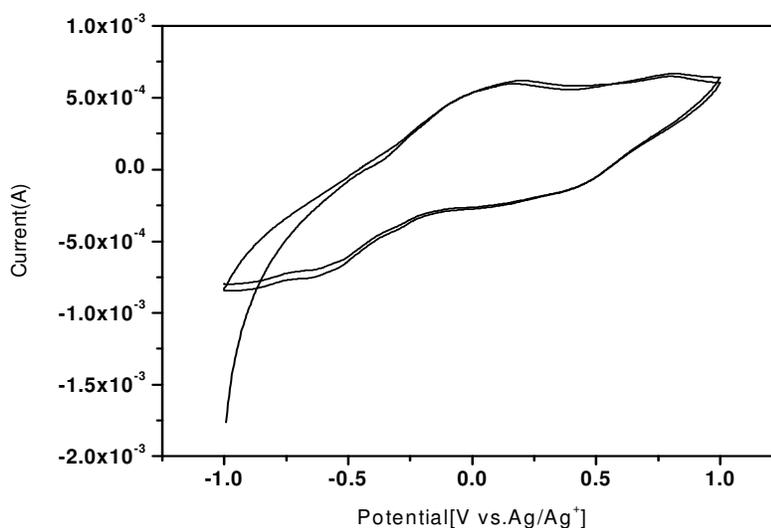


Figure 8(b). Cyclic voltammogram of O₂ treated lithium vanadate (pH= 2, precipitation method) in non-aqueous electrolyte (1M LiClO₄ dissolved in propylene carbonate) with scan rate 5mV/s.

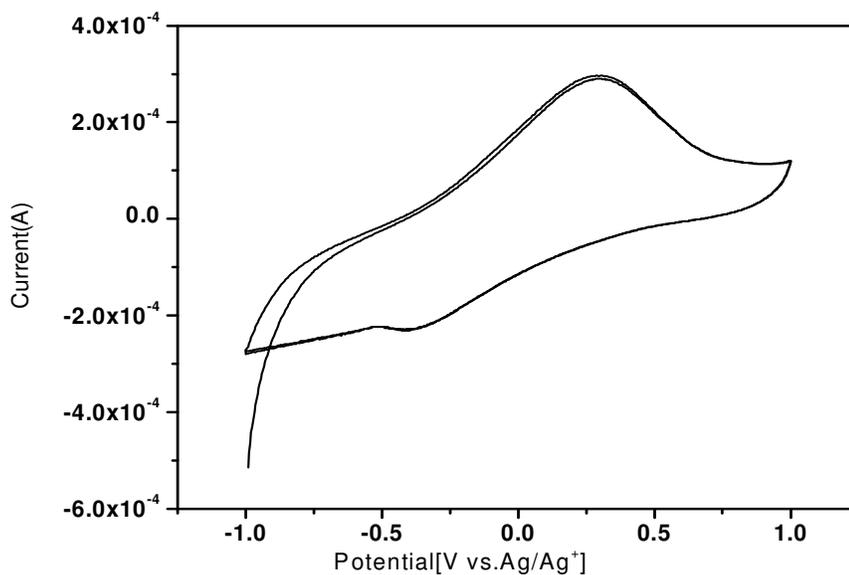


Figure 8(c). Cyclic voltammogram of lithium vanadate (pH= 6, precipitation method) in non-aqueous electrolyte (1M LiClO₄ dissolved in propylene carbonate) with scan rate 5mV/s.

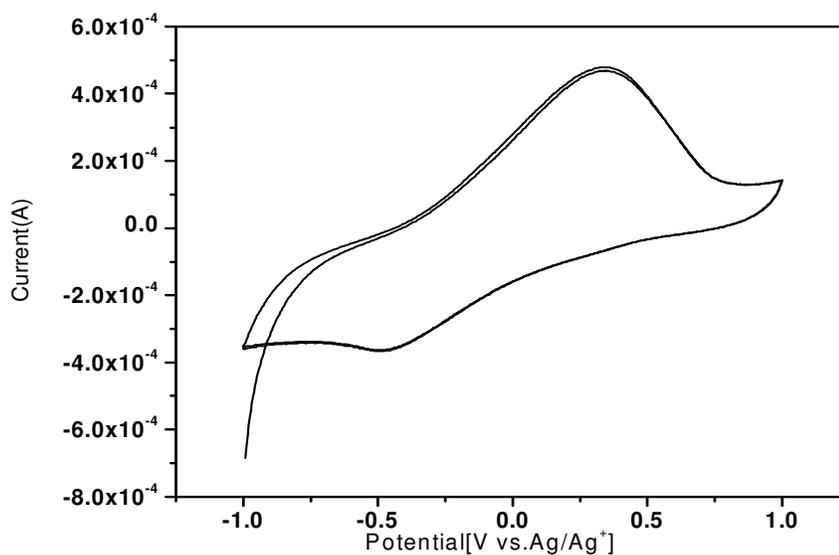


Figure 8(d). Cyclic voltammogram of O₂ treated lithium vanadate (pH= 6, precipitation method) in non-aqueous electrolyte (1M LiClO₄ dissolved in propylene carbonate) with scan rate 5mV/s.

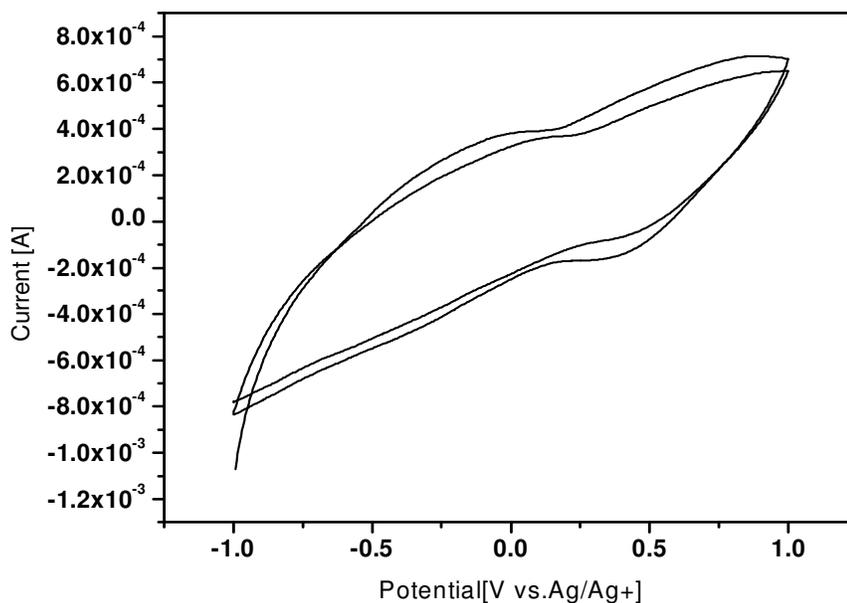


Figure 8(e). Cyclic voltammogram of lithium vanadate (pH= 2, hydrothermal method) in non-aqueous electrolyte (1M LiClO₄ dissolved in propylene carbonate) with scan rate 5mV/s.

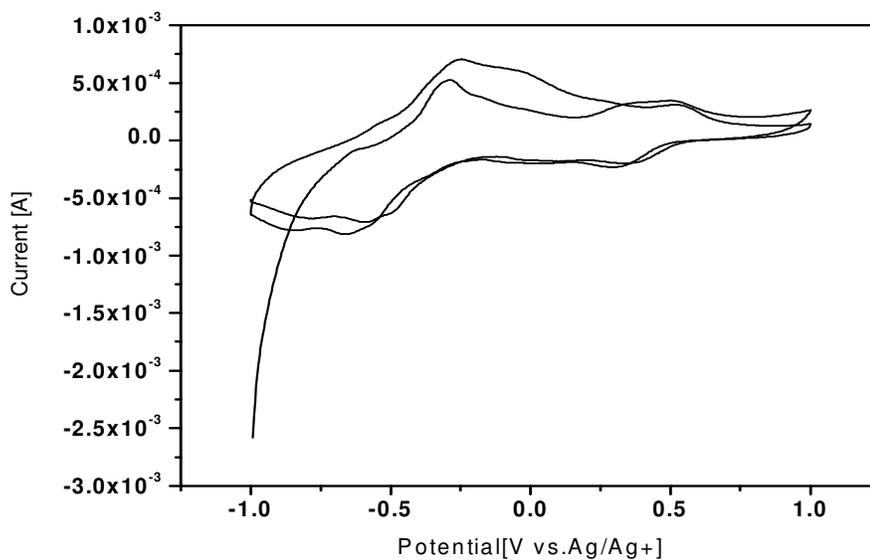


Figure 8(f). Cyclic voltammogram of lithium vanadate (pH = 6, hydrothermal method) in non-aqueous electrolyte (1M LiClO₄ dissolved in propylene carbonate) with scan rate 5mV/s.

4. CONCLUSIONS

Nanosized $\text{LiVO}_3/\text{Li}_4\text{V}_{10}\text{O}_{27}$ was synthesized by a precipitation method using lithium vanadate solutions with pH=2 and 6. The O_2 -treated samples prepared by the precipitation method from the solutions of pH = 2 and 6 were identified as $\text{LiVO}_3/\text{Li}_3\text{VO}_4$. LiV_3O_8 Nanobelts were prepared by hydrothermally using lithium vanadate solutions of pH =2 and 6. The precipitation method can be applied for large-scale production of low-dimensional nanostructured lithium vanadium oxides. The electrochemical measurements clearly show the Li^+ intercalation and deintercalation into/from the electrodes made of nanosized lithium vanadates.

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