

# Novel synthesis of high-capacity cobalt vanadate for use in lithium secondary cells

Yong Top Kim<sup>a</sup>, Gopukumar<sup>a,1</sup>, Kwang Bum Kim<sup>a,\*</sup>,  
Byung Won Cho<sup>b</sup>

<sup>a</sup>*Division of Materials Science and Engineering, Yonsei University, 134 Sinchon-dong, Saedemoun-gu, 120-749 Seoul, South Korea*

<sup>b</sup>*Eco & Nano Research Center, Korea Institute of Science and Technology, Seoul, South Korea*

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## Abstract

The mild combustion synthesis of cobalt vanadate involving the reaction of  $V_2O_5$ ,  $Co(NO_3)_2$  and glycine as starting materials is reported. The synthesized material is annealed at 550 °C and characterized by means of X-ray diffraction (XRD), cyclic voltammetry, and galvanostatic charge–discharge cycling techniques. XRD analysis indicates that the structure of the synthesized cobalt vanadate is amorphous. The initial delivered capacity is  $\sim 275 \text{ mAh g}^{-1}$  in a  $Li//CoV_2O_5$  cell at a current density of  $0.05 \text{ mA cm}^{-2}$  when cycled between 2 and 4 V using 1 M  $LiClO_4$  in propylene carbonate as electrolyte. The capacity remains stable even after 10 cycles. The cobalt vanadate prepared by this new synthetic route is, therefore, a potential candidate for lithium secondary batteries.

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**Keywords:** Cobalt vanadate; Glycine; Capacity; Cycle-life; Lithium battery

## 1. Introduction

Rechargeable lithium batteries have been the focus of attention since the 1980s as they offer high voltage, good low temperature performance, easy handling, etc. [1,2]. Moreover, the batteries find use in a variety of applications, viz. medical implants, cell-phones, electronic toys, electric vehicles [3,4]. Many workers around the world are pursuing extensive research for the development of high-voltage and high-capacity positive-electrode (cathode) materials for use in such batteries [5,6]. Possible cathode materials include lithiated transition metal oxides, vanadium oxides, manganese oxides, molybdenum oxides, and titanium sulfides [7,8]. Among these materials, vanadium oxides [9,10] are attractive in view of their high lithium-storage capabilities and, therefore, high capacities.

Various types of vanadium oxides, such as quasi-layered  $\alpha$ - $V_2O_5$  lithiated derivatives, have been extensively investi-

gated since 1976 [11–13]. Such investigations have revealed that poorly crystalline or amorphous varieties of  $V_2O_5$  exhibit good electrochemical behavior, and recent studies have been reported with xerogels, aerogels and electrolytic forms of  $V_2O_5$ . The use of pure  $V_2O_5$  in lithium secondary batteries leads to capacity fading [14] on cycling and, therefore, efforts to stabilize the structure for better cycle-ability is underway in many laboratories. Attempts to enhance the reversibility of  $V_2O_5$  have included low-temperature synthesis and the incorporation of transition and non-transition metals into the  $V_2O_5$  structure [15,16].

Recently, Andrukaitis et al. [17–19] have highlighted the effect of metal ions (Co, Ni, Mn, Na, Cu and Al) incorporated in vanadium-based oxides as cathode materials in lithium batteries. Their investigations revealed that either Co- or Cu-based vanadium oxide materials exhibit superior electrochemical performance in lithium cells. Metal-based vanadium oxides have been synthesized by several techniques, e.g. hydrothermal, solid-state, precipitation, electrodeposition, ion-exchange techniques [20–22]. Even though all these approaches have yielded good lithium intercalating cathode materials, these are several disadvantages such as low working voltages ( $<1$ ), long processing time, the requirement of accurate pH control and, in some cases

\* Corresponding author. Fax: +82-2-312-5375.

E-mail addresses: deepika41@hotmail.com (Gopukumar), kbkim@yonsei.ac.kr (K.B. Kim).

<sup>1</sup> On study leave from Central Electrochemical Research Institute (CSIR), Karaikudi, India.

involve, cumbersome processing. Hence, it is worthwhile to explore new synthesis techniques for preparing cobalt vanadates, while preserving or enhancing their electrochemical behavior. Therefore, this study presents a new method previously not attempted for the synthesis of cobalt vanadate using glycine as a chelating and combustion agent. Further, the electrochemical nature of lithium intercalation/de-intercalation in the synthesized cobalt vanadate is investigated and compared with that of  $\omega$ - $\text{Li}_3\text{V}_2\text{O}_5$ , the best vanadium cathode material reported to date [23].

## 2. Experimental

Stoichiometric amounts of high-purity  $\text{V}_2\text{O}_5$ ,  $\text{Co}(\text{NO}_3)_2$  and glycine (Aldrich) were dissolved in distilled water and the solution was initially heated to  $80^\circ\text{C}$ , followed by heating to  $135$  and  $235^\circ\text{C}$ . Finally, the products were mixed thoroughly and annealed at  $550^\circ\text{C}$ . A schematic view of the preparation method is given in Fig. 1. Inductively coupled plasma (ICP)–AES analysis was performed on the synthesized powders to confirm the stoichiometry of cobalt and vanadium. The ratio of Co:V was found to be 1:2.

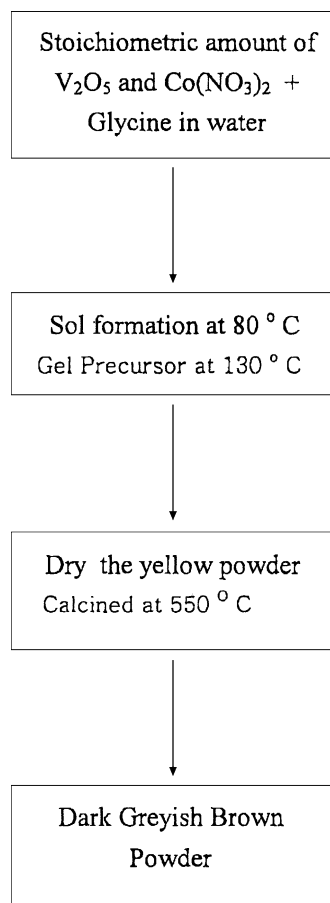


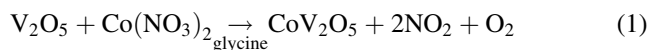
Fig. 1. Flow chart of synthesis procedure.

The structures of the prepared powders were evaluated with an automated Rigaku powder X-ray diffractometer using  $\text{Cu K}\alpha$  radiation by measuring the diffraction angle ( $2\theta$ ) between  $10$  and  $70^\circ$  with an increment of  $0.02^\circ \text{ min}^{-1}$ . X-ray diffraction of a discharged electrode in a  $\text{Li}/\text{CoV}_2\text{O}_5$  cell was also performed to determine changes in structure.

Electrochemical measurements were carried out using a three-electrode glass cell with metallic lithium as counter and reference electrodes. The working electrode consisted of the synthesized cobalt vanadate mixed powder coated on an aluminum current-collector. The powder mix in the working electrode was 85% cobalt vanadate, 15% acetylene black and 5% PVDF binder blended with NMP solvent. Cyclic voltammetric (CV) measurements were carried out at a sweep rate of  $10 \mu\text{V s}^{-1}$  in  $1 \text{ M LiClO}_4$ , propylene carbonate (PC), as electrolyte solution in the potential range  $2$ – $4 \text{ V}$ . Galvanostatic charge–discharge cycling experiments were performed using an automatic battery cycle-life tester.

## 3. Results and discussion

The chemical reaction for the synthesis of cobalt vanadate can be expressed as:



The addition of glycine favors the formation of a glycine cobalt gel by chelating with cobalt. It also acts as a self-igniting combustion agent and thereby results in the formation of cobalt vanadate.

The XRD patterns of the starting vanadium oxide ( $\text{V}_2\text{O}_5$ ) and the synthesized cobalt vanadate are presented in Fig. 2. The crystallinity, indicated by sharp high-intensity peaks in the parent  $\text{V}_2\text{O}_5$ , has more or less disappeared into very few low-intensity peaks in the synthesized cobalt vanadate. This suggests that the latter has an amorphous structure. A similar loss of crystallinity was observed by Delmas et al. [23] from

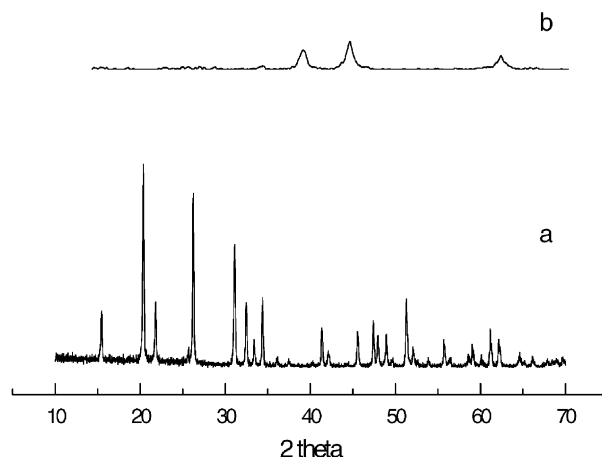


Fig. 2. XRD patterns of (a) parent  $\text{V}_2\text{O}_5$  and (b) synthesized  $\text{CoV}_2\text{O}_5$ .

studies on metal-incorporated  $V_2O_5$ . Further, it has been suggested by West et al. [24] that the low-intensity peaks indicate a near-amorphous structure which decreases the lithium diffusion path lengths in the materials and thereby leads to enhanced electrochemical characteristics. Moreover, it has been observed that the structure is dependent on the synthesis procedure and the temperature of annealing. Andrukaitis et al. [17] investigated the effect of annealing temperature on the performance of metal-substituted vanadium oxides ( $MV_2O_6$ , where  $M = Mn, Co, Ni, Zn$ ) and found that the capacity output at lower temperatures is greater than that at higher temperatures. Similar results were also reported by Sakurai and Yamaki [25] for copper-substituted vanadium oxides. The effect of the high- and low-temperature annealing on the electrochemical behavior of the vanadates was also highlighted by the studies of Dai et al. [26] using XRD and SEM techniques. It was argued that low-temperature annealing results in small crystallites which give rise to either broad or low-intensity peaks. On the other hand, high-temperature annealing leads to sharp peaks with high intensities. Furthermore, the particle orientation and lower diffraction peaks have been attributed to the synthesis technique employed which produces strained puckered vanadates.

Following the above discussion, we observe that the synthesized cobalt vanadate powders possess few crystallites with very low-intensity diffraction peaks compared with the parent crystalline  $V_2O_5$ . Therefore, we can postulate that during the formation of cobalt vanadate,  $NO_2$  and  $O_2$  are evolved and that these molecules may be inserted or extracted into  $V_2O_5$  layers. This could result in differently orientated and strained  $V_2O_5$  layers which lead to kinetically stable cobalt vanadates. Further, intercalation of these molecules could also give rise to larger inter-layer distances as proposed by Maney et al. [27] in a study of vanadates. Subsequent removal of these intercalated molecules preserves the larger inter-layer distances by maintaining the strain. This orientation could possibly enhance the performance of the presently synthesized cobalt vanadate as compared with pure  $V_2O_5$ , as described elsewhere in this study.

Cyclic voltammograms of the synthesized cobalt vanadate powder are shown in Fig. 3. The shape of the voltammogram is that for  $V_2O_5$  [29]. Lithium insertion and extraction peaks into cobalt vanadate can be identified around 3.25 and 3.20 V, respectively. Further, there is no fading on subsequent cycling and this demonstrates good reversibility of the synthesized material. The following reaction mechanism can be formulated for the observed electrochemical processes:



The oxidation and reduction peaks are not well pronounced. This can be assigned to low crystallinity and the near-amorphous nature which results from strained layered structures.

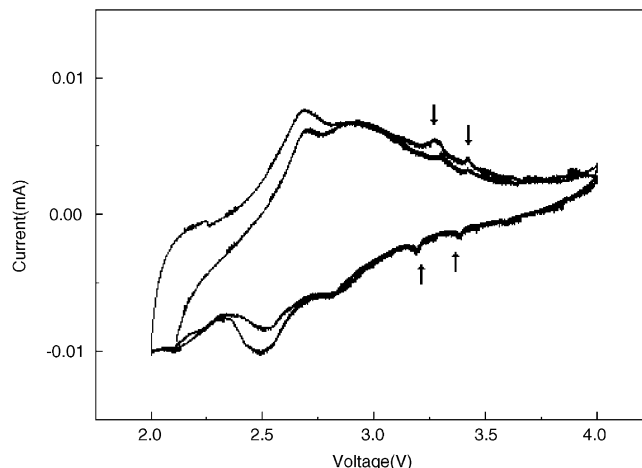
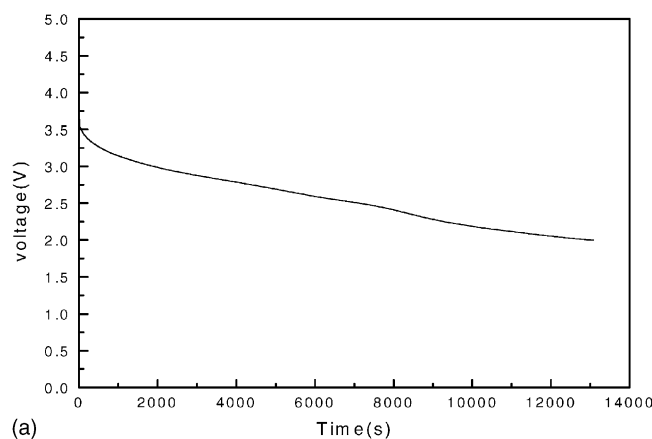
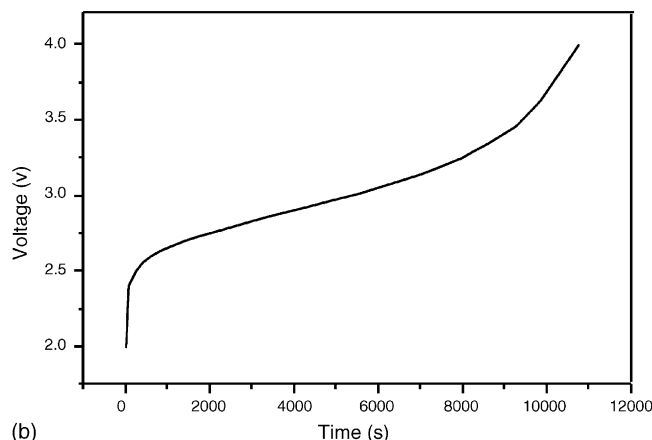


Fig. 3. Cyclic voltammograms of  $CoV_2O_5$ .

The discharge behavior of  $Li//CoV_2O_5$  in a 1 M  $LiClO_4/PC$  electrolyte and discharged at a current density of  $0.05 \text{ mA cm}^{-2}$  from 3.5 to 2 V is shown in Fig. 4(a). The open-circuit voltage (OCV) of the cell is 3.50 V. It is observed from the discharge curve that the incorporation of lithium into the cobalt vanadate proceeds smoothly with an average operating voltage of around 2.5–2.75 V. As there



(a)



(b)

Fig. 4. Discharge (a) and charge (b) behavior of  $Li//CoV_2O_5$  cell.

is no sudden fall at the end of discharge (2 V), it can be said that the cell could operate to lower cut-off voltages. The present study, however, concerned on investigation of high-voltage cycleability and, therefore, the cut-off voltage was fixed at 2 V. The charging curve (Fig. 4(b)) shows that there is an initial increase in voltage from 2 to 2.5 V due to polarization of the electrodes. Thereafter, the extraction of lithium from the cobalt vanadate proceeds progressively up to 3.40 V followed by a steep increase up to 4 V. The steep increase beyond 3.40 V can be assigned to  $V^{5+}$  and is similar to the observations of Dai et al. [26] in a study on lithium vanadates.

The cycleability of the fabricated Li//CoV<sub>2</sub>O<sub>5</sub> cells was also investigated by galvanostatic discharge–charge cycling at a current density of 0.05 mA cm<sup>-2</sup> in 1 M LiClO<sub>4</sub>/PC electrolyte. The results are presented in Fig. 5. The first charge is only around 7 mAh g<sup>-1</sup> and this is understandable as the present cell is a lithium cell and is already in a charged state with an open-circuit voltage of 3.50 V. Moreover, the steep increase to 4 V can be ascribed to  $V^{5+}$ . The discharge capacity approaches 300 mAh g<sup>-1</sup> in first 2 cycles, and from the third cycle onwards stabilizes at 275 mAh g<sup>-1</sup> up to the investigated 10 cycles. The loss in capacity of 20–25 mAh g<sup>-1</sup> during the first two cycles can be ascribed to the irreversible extraction of Li<sup>+</sup> ions from cobalt vanadate. The charge and discharge capacities are identical beyond second cycle. This indicates that the amount of lithium intercalated is equal to the amount of lithium extracted, i.e. the synthesized material demonstrates excellent cycleability. As described earlier, the enhanced electrochemical performance of the synthesized cobalt vanadate is due to a strained V<sub>2</sub>O<sub>5</sub> structure coupled with increased inter-layer distances.

Comparison of the present results with previously reported [17–19] investigations of lithium insertion into metal vanadates (Co, Mn, Cu and Zn) with respect to specific capacity, average working voltage and specific energy are presented in Table 1. The data show the superior nature of the investigated cobalt vanadate. Andrukaitis et al. [17] have found that cobalt vanadate presents improves the performance with respect to capacity and specific energy. The results of Sakurai and Yamaki [25] on copper vanadate are more impressive; the specific energy is 1.34 Wh g<sup>-1</sup> and is higher than that of Co, Mn, Ni and Zn vanadates. In spite of

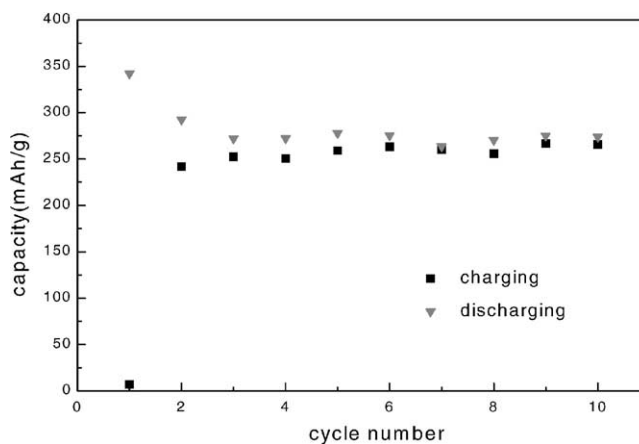


Fig. 5. Cycling behavior of Li//CoV<sub>2</sub>O<sub>5</sub> cell.

the excellent specific energy cobalt and copper vanadates, the average working voltage is 1.5 and 2.25 V, respectively. The cut-off voltage is as low as 1 or 1.2 V. In view of the low cut-off voltage, Sakurai and Yamaki [25] obtained higher capacities, thereby higher specific energies, than in the present study. It is interesting to note that the synthesized cobalt vanadate reported here has a higher operating voltage of 2.45–2.50 V than those reported earlier, i.e. around 1.5 or 2.25 V. Further, a stable capacity of 275 mAh g<sup>-1</sup> at a cut-off voltage of 2 V is obtained, which gives a high specific energy of 0.69 Wh g<sup>-1</sup>. The results are higher than those reported earlier both in terms of capacity and working voltage. Moreover, it can be seen that about 2.4 Li per formula weight of cobalt vanadate can be intercalated, which is clearly superior to 3 Li per formula weight of copper vanadate given the lower cut-off voltage with this material. Very recently, the investigations of Legagneur et al. [28] of the lithium intercalation properties of sodium vanadium oxides (Na<sub>0.9</sub>H<sub>0.1</sub>V<sub>3</sub>O<sub>8</sub>) has suggested that stable capacities of 260 mAh g<sup>-1</sup> could be obtained at low current drains, which is comparable with 240 mAh g<sup>-1</sup> for ω-Li<sub>3</sub>V<sub>2</sub>O<sub>5</sub>, the best positive vanadate material available to date. By contrast, the synthesized cobalt vanadate material examined in the present study delivers a higher stable capacity of ~275 mAh g<sup>-1</sup> at low current density with excellent cycleability. Hence, the material is a candidate material for practical lithium batteries.

Table 1  
Comparison of various transition metal vanadates

Cathode material	Annealing temperature (°C)	Specific capacity (Ah g <sup>-1</sup> )	Average discharge voltage (V)	Cut-off voltage (V)	Specific energy (Wh g <sup>-1</sup> )
MnV <sub>2</sub> O <sub>6</sub>	550	0.300	1.46	1.0	0.438
CoV <sub>2</sub> O <sub>6</sub>	550	0.327	1.55	1.0	0.500
NiV <sub>2</sub> O <sub>6</sub>	550	0.260	1.5	1.0	0.390
CuV <sub>2</sub> O <sub>6</sub>	550	0.596	2.25	1.2	1.341
ZnV <sub>2</sub> O <sub>6</sub>	550	0.172	1.9	1.0	0.326
CoV <sub>2</sub> O <sub>5</sub>	550	0.275	2.5	2.0	0.688

#### 4. Conclusions

A novel cobalt vanadate has been synthesized by means of a glycine assisted, sol–gel combustion technique. Cyclic voltammetric studies indicate the intercalation/de-intercalation of lithium into the cobalt vanadate structure. A high operating voltage of 2.45–2.50 V and excellent cycleability are added features of the investigated material. The synthesized cobalt vanadate exhibits a high, stable, charge–discharge capacity of  $\sim 275 \text{ mAh g}^{-1}$  with no capacity fading, even after 10 cycles, and a high specific energy of  $0.69 \text{ Wh g}^{-1}$ . The amorphous nature of the synthesized cobalt vanadate powder which is due to a strained cobalt vanadate structure with increased inter-layer distance and different crystallite orientation, can be beneficial for lithium intercalation/de-intercalation from the positive electrode and thereby show enhanced electrochemical performance.

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