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# Use of pure and cobalt-added aluminum vanadates as cathodes in lithium rechargeable cells

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## Abstract

The aluminum vanadates,  $\text{Al}_x\text{V}_6\text{O}_{13+y}$ , were found to reversibly intercalate lithium. These vanadates were found to deliver reversible specific capacities in the range of 100–300 mAh/g, with average voltages of 2.3–2.5 V, where  $0.1 < x < 1.0$ . The efficiency of reversible insertion depended on the stoichiometric ratio of Al:V in the vanadate structure. Stable rechargeable performance was obtained by the incorporation of small amounts of aluminum in the cobalt vanadates ( $\text{Co}(\text{VO}_3)_2$ ). Specific capacities in the range of 200–400 mAh/g, with average voltages of 2.4 V for  $\text{Al}_x\text{Co}_3\text{V}_6\text{O}_{13+y}$  (where  $0 < x < 2$  and  $3 < y < 8$ ) were achieved. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium insertion; Aluminum vanadate; Vanadate; Transition metal oxides; Vanadium oxide

## 1. Introduction

Recent work on transition metal vanadate cathodes prepared using low-temperature synthesis techniques has shown favorable specific capacities for use in lithium batteries [1–4]. The first row transition metal vanadates,  $\text{Me}_x(\text{VO}_3)_2$ , reversibly intercalate lithium ions, and were found to have good initial specific capacity with average operating voltages in the range of 1.4–2.3 V [4]. They worked well for a lithium primary cell application, yielding over 1.5 Wh/g, one of the largest specific energies for a vanadate material [5]; however, for a rechargeable application, they displayed significant capacity fade over the first few cycles. This limited their practical use in rechargeable lithium cells, since a higher specific capacity is needed to offset the lower operating voltages.

The use of non-transition metal vanadates, such as alkali metal vanadium oxides ( $\text{M}_x\text{V}_6\text{O}_{13+y}$ , where  $\text{M} = \text{K}, \text{Rb}, \text{or Cs}$ ) has been shown to offer better cycling behavior than the pure vanadium oxides [6]. This paper examines the use of Al in vanadates prepared using low-temperature synthesis techniques of electrodeposition or precipitation. Certain stoichiometries of  $\text{Al}_x\text{V}_6\text{O}_{13+y}$  show a more stable cycling performance with little capacity fade over the first 50 cycles.

The increased amount of aluminum in the vanadate, however, does diminish the specific capacity, and a balance between cycle stability and specific capacity occurs. Incorporation of aluminum in the cobalt vanadates was also examined. The cobalt vanadates were found to be the most promising when small amounts of Al are included in the vanadate.

## 2. Experimental

### 2.1. Preparation of cathode materials

The preparation for aluminum vanadates by the precipitation method was similar to the preparation of transition metal vanadates described elsewhere [5]. In this case, 1.0 M aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) was added to 0.5 M  $\text{NH}_4\text{VO}_3$  in various Al:V molar ratios in the range from 1:3 to 1:10. The aqueous mixtures were heated at 80°C for several hours, and the precipitated material collected and washed with distilled water, then allowed to dry in an oven overnight at 70°C. For the preparation of Al–Co vanadates, 1.0 M aluminum sulfate was first added to a 0.5 M solution of the cobalt nitrate,  $\text{Co}(\text{NO}_3)_2$ , with Co:V molar ratios in the range from 1:2 to 1:3. This mixture was then added to the  $\text{NH}_4\text{VO}_3$ , heated at 80°C for several hours, and the precipitated material collected and washed with distilled water and dried at 70°C overnight.

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The electrochemical preparation was similar to the method used for the formation of alkali metal vanadates by cyclic voltammetry described elsewhere [6]. The aluminum sulfate was not added to the 50°C  $\text{NH}_4\text{VO}_3$  solution until the cell had been cycled for at least 1 h (a color change was observed in the solution). The electrodeposited materials were collected, washed in distilled water, and allowed to dry overnight in an oven at 70°C. The materials were analyzed by atomic absorption (AA), chemical analysis, powder X-ray diffraction (XRD), and differential scanning calorimetry (DSC) methods. The powders were then heated at 350°C for 24 h under argon and then analyzed.

## 2.2. Electrochemical measurements

The preparation of electrodes involved first mixing the active material with 10 wt.% carbon and 5 wt.% polyvinylidene fluoride (PVDF) binder in 1-methyl-2-pyrrolidione (*n*-mp), using a mortar and pestle to make a slurry. The *n*-mp was added as needed during mixing. The slurry was spread on an aluminum or copper sheet using a doctor blade (set between 50 and 350  $\mu\text{m}$ ). The wet cast was left in a convection oven at 60°C until it appeared dry. A disc of 1.3 cm diameter was cut from the cast and then pressed at 17 MPa at 25°C. The pressed disk can range from approximately 50 to 150  $\mu\text{m}$  in thickness, including the aluminum current collector. Coin cells were then assembled using an electrolyte composed of 1 M  $\text{LiPF}_6$  dissolved in 1:1 of ethylene carbonate and dimethyl carbonate (EC:DMC) and a counter electrode of Li metal. The cells were cycled continuously at a rate of about 20 mA/g for discharging and 10 mA/g for charging to approximate *C*/20 and *C*/40 discharge/charge rates. Voltage and specific capacity were measured using an ARBIN Instruments BT2020 Cycler.

## 3. Results

### 3.1. Physical and chemical analyses

Two different preparation methods were used in this study to determine which one provided the most usable materials for use as a cathode. The advantage with the electrodeposition technique is that no binders or carbon is necessary, because the material is directly deposited onto a conducting substrate. Also, materials formed this way are more crystalline, with fewer impurities, compared to the precipitation technique. Unfortunately, it proved difficult to form large quantities of adherent electrodeposits of the aluminum vanadates which had been accomplished for the alkali metal vanadate bronzes ( $\text{M}_x\text{V}_6\text{O}_{13+y}$ ,  $\text{M} = \text{K}, \text{Rb}, \text{or Cs}$ ) [6]. Enough electrodeposited material was collected by scraping it off the electrode for analysis and making coin cells. Analysis found that the electrodeposited vanadates had only small amounts of the  $\text{Al}^{3+}$  ion included in the structure, with the stoichiometry,  $\text{Al}_x(\text{NH}_4)_{4-x}\text{V}_6\text{O}_{16}$ , where  $0.0 < x < 1.0$ .

With heating the electrodeposited material above 350°C,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are removed into the gas stream to leave the solid product  $\text{Al}_x\text{V}_6\text{O}_{13+y}$ , where  $0.0 < x < 1.0$  and  $0.1 < y < 3.0$ . The reactions are similar to the formation of alkali metal vanadium oxides described elsewhere [6].

Analysis of the vanadates made by the precipitation methods with only aluminum present, from atomic absorption and chemical analysis, had stoichiometries of  $\text{Al}_x\text{V}_6\text{O}_{13+y}$ , where  $1.0 < x < 2.0$  and  $1.5 < y < 3.5$ . Using a mixture of Al and Co, it was possible to produce a range of Al–Co vanadates with the general stoichiometry  $\text{Al}_x\text{Co}_3\text{V}_6\text{O}_{13+y}$ , where  $0 < x < 2$  and  $3 < y < 8$ . X-ray diffraction spectroscopy indicated that the materials had a range of crystallinity with most samples being semi-crystalline in nature. As the value of *x* became larger, the vanadates became less crystalline. The advantage of the precipitation method is the ease of making large amounts of vanadate materials on a large scale, with the ability to use one or more transition metals in a potentially large range of stoichiometries. Further work on doping smaller amounts of aluminum and other metals into the vanadates using this technique is needed.

### 3.2. Electrochemical results

On average, specific capacities in the range of 0.2–0.4 Ah/g were obtained for the first discharge to a 1.5 V cut-off (see Fig. 1). The Al vanadates,  $\text{Al}_x\text{V}_6\text{O}_{13+y}$ , were found to reversibly insert and remove Li in a voltage range of 3.5–1.5 V. Although, specific capacities were not initially as high as that of some transition metal vanadates, the Al vanadates did have superior cycling performance and less capacity fade for  $x < 1.0$  (see Fig. 2). The Al vanadates formed by the precipitation technique contained higher amounts of Al in the vanadate structure and had significantly poorer specific capacities when the value of *x* > 1.0. Synthesis of lower Al content vanadates via the precipitation method proved difficult and an electrodeposition method was used as well.

For vanadates containing only Al, the specific capacity actually shows a recovery after an initial loss of 1/3 its initial capacity to almost 90% of the first discharge by the 10th and subsequent cycles. This behavior was unlike previous transition metal vanadates examined, where up to 1/2 of the capacity could be irretrievably lost after the first few cycles [7]. This was believed to be due, in large part, to phase changes that occurred in the vanadate structure. Although, very little capacity fade occurred for cycling the higher content Al vanadates, the low specific capacity made them unsuitable for practical use in lithium batteries.

The most probable reason for the poor specific capacity is the fact that Al ions are inactive with respect to the lithium-insertion process and thus, in effect, block this process from occurring effectively in the vanadate structure. This was explained as a problem for the alkali metal vanadium bronzes as well. When too much of the alkali metal ion was present, it had an adverse effect on the specific capacity of the bronze [6]. The results show similar behavior to the

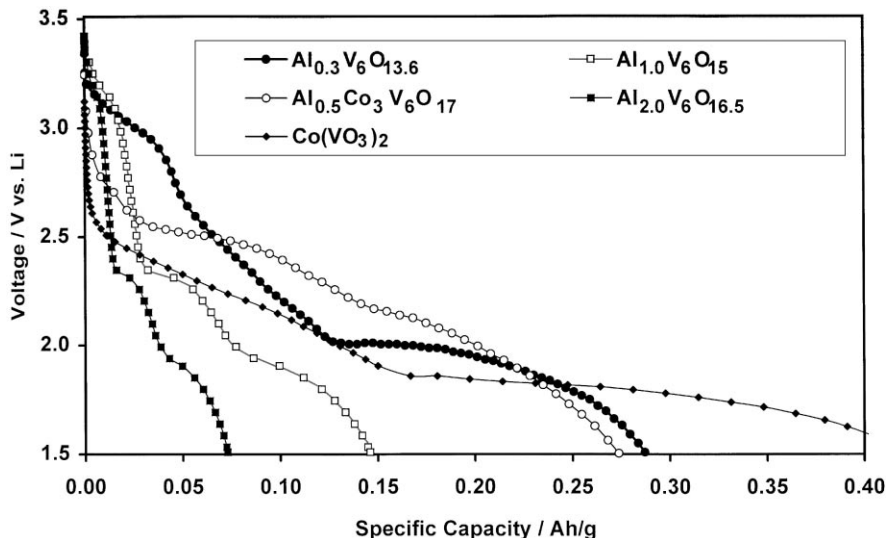


Fig. 1. Plot of the voltage vs. the specific capacity for the initial discharge of a coin cell with various  $\text{Al}_x\text{V}_6\text{O}_{13+y}$  and  $\text{Al}_x\text{Co}_3\text{V}_6\text{O}_{13+y}$  electrodes, Li metal anode, and 1 M  $\text{LiPF}_6$  in 1:1 EC:DMC electrolyte.

alkali metal bronzes, where Al now takes the place of the alkali metal in the bronze structure. Results of constant current discharge/charge and cyclic voltammetry show phase changes that have been observed for alkali metal bronzes. Further study would be required to determine if any clear advantage would be obtained by the use of the Al-containing vanadate over the other bronzes. Given the difficulty in producing large amounts of Al vanadate materials by the electrodeposition technique, the use of alkali metal bronzes has a distinct advantage.

Cobalt vanadates studied previously had structural changes occurring on the second and subsequent cycles, and the discharge curve became smooth and free of phase

changes [7]. However, the presence of Al helps these vanadates to maintain their structural integrity. As seen in Fig. 2, if the Al content is  $x = 0.5$  in the cobalt hexavanadate, the specific capacity fades only 1.5% in the first 10 cycles compared to about 40% for the cobalt vanadate. Also, cycling beyond 40 or more cycles, the specific capacity is similar and gradually improves for the Al cobalt vanadate relative to the Co vanadate. The Al vanadates heated at  $350^\circ\text{C}$  are semi-crystalline and as can be seen in the cyclic voltammograms in Fig. 3, the Al–Co vanadate retains similar phase changes for the 2nd and 25th cycles. More investigation into optimizing the aluminum content in the vanadate needs to be done.

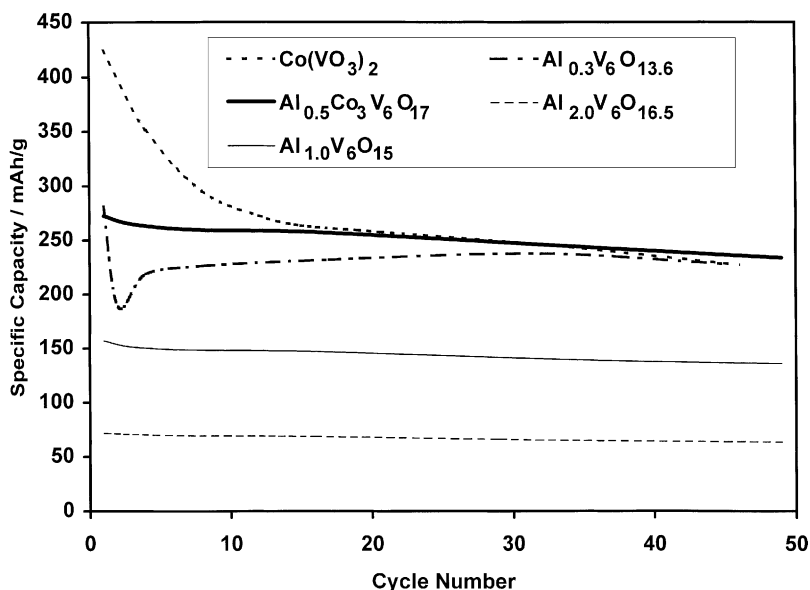


Fig. 2. Plot of the specific capacity for active cathode material of various vanadates cycled at a  $C/10$  rate to a 1.5 V discharge cut-off.

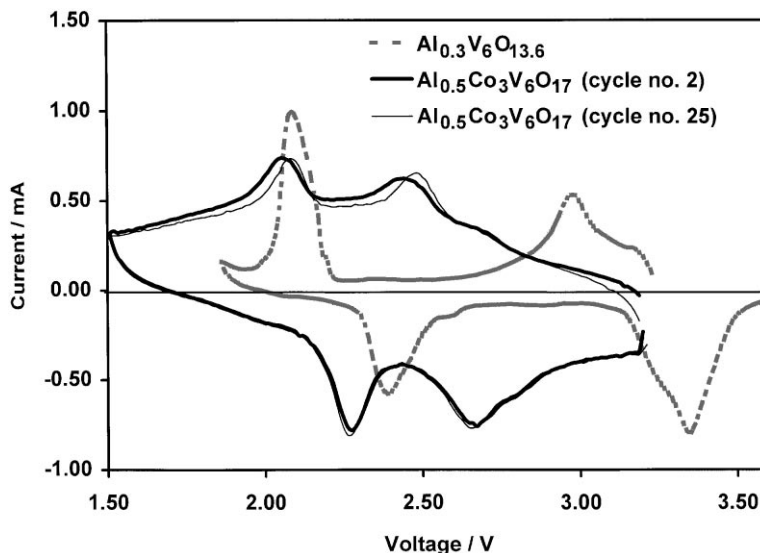


Fig. 3. CV for the discharge and charge of a coin cell with  $\text{Al}_x\text{V}_6\text{O}_{13+y}$  and  $\text{Al}_x\text{Co}_3\text{V}_6\text{O}_{13+y}$  electrode, Li metal anode, and 1 M  $\text{LiPF}_6$  in 1:1 EC:DMC electrolyte.

#### 4. Conclusions

By the addition of Al in cobalt vanadate, the overall cycle life improved with very little capacity fade, as seen with the pure Al and Co vanadates. The specific capacities were higher than for the Al vanadate, but lower than the initial specific capacities obtained for cobalt vanadates previously studied [5], and dependant on the amount of Al present.

If the amount of inactive metals such as Al or alkali metals such as K can be added in small amounts to vanadium oxides, there is a beneficial effect to the reversible insertion of lithium in the vanadates studied. The cycle life and capacity fade of these materials can be improved with a small sacrifice in initial specific capacity. Their presence appears to limit the structural changes that occur with repeated cycling that leads to cathode solubility issues that commonly occur with many of the vanadate electrodes in the

non-aqueous electrolytes being used for lithium batteries. It is felt that with the proper coupling of anode/cathode combinations with these types of vanadates, there is potential use in lithium cells with aqueous electrolytes.

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