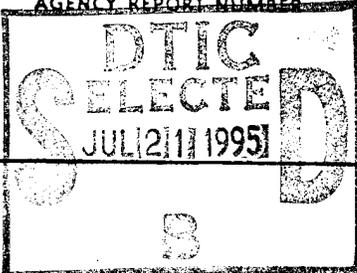


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by

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# Lithium Intercalation in Vanadium Pentoxide Aerogels

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## ABSTRACT

Vanadium pentoxide ( $V_2O_5$ ) aerogels were prepared by supercritical drying of a vanadyl alkoxide precursor. Thin films prepared from the aerogel were found to intercalate up to 1.9 moles of Li per mole of aerogel with good cycling reversibility.

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Vanadium oxides have been studied for over a century, however, in recent years there has been renewed interest in these materials because of their interesting electrical and optical properties.<sup>1</sup> Several different vanadium oxide compositions are of interest as insertion electrodes for secondary lithium batteries because of their reversible lithium intercalation properties.<sup>2</sup> Vanadium pentoxide ( $V_2O_5$ ) is one of these compositions and the electrochemical properties of vanadium pentoxide xerogels ( $V_2O_5 \cdot n H_2O$ ) have shown considerable promise.<sup>2,3</sup> An attractive feature of these materials is that they are readily prepared as films or powders by sol-gel methods through the protonation of an ion exchanged sodium metavanadate solution.<sup>1</sup> Recently, researchers have shown that up to 3 moles of lithium can be intercalated per mole of  $V_2O_5 \cdot 0.5 H_2O$ .<sup>4</sup>

Xerogels are formed when the liquid phase filling the pores of a wet gel evaporates causing the partial collapse of the gel network and some densification.<sup>5</sup> It is common for xerogels to possess porosities in the range of 50%. An alternative method for removing the pore liquid is to use supercritical extraction. In this case the gel network remains essentially intact, there is very little pore collapse and a highly porous material, termed an aerogel, is produced. Aerogels are characterized by a porosity in excess of 90% and extremely high surface areas (several hundred  $m^2/g$  to over 1000  $m^2/g$ ).<sup>5</sup> They have been used in the catalyst field because of their elaborate pore structure and high surface areas.<sup>6</sup> Much of the prior work with aerogels has been devoted to silica based systems and other electrically insulating oxides. With the exception of carbon aerogels, the electrochemical properties of aerogels have not yet been explored.<sup>7</sup>

Previous work on the synthesis of vanadium pentoxide aerogels (VAG) suggested that the fine colloid size, high surface area (300  $m^2/g$  to 400  $m^2/g$ ) and controllable porosity makes these materials excellent candidates for lithium insertion electrodes.<sup>8</sup> This paper presents results on the lithium intercalation properties of VAG films prepared from an alkoxide precursor and supercritically dried using  $CO_2$ .

## Experimental

Monolithic VAG samples were prepared by supercritical drying with liquid CO<sub>2</sub>. The alkoxide precursor, vanadyl triisopropoxide, VO(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> (Gelest, Inc.), was hydrolyzed in acetone-water solutions and condensed to form a "wet gel". The molar ratio of the sol components was 1/30/15 (VO(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> /water/acetone). The wet gels were aged for 3 days and then washed in anhydrous acetone to ensure complete replacement of the initial acetone mixture. The acetone-exchanged gels were then transferred to an autoclave (Polaron E3000 Critical Point Dryer) for supercritical extraction by CO<sub>2</sub>. The samples were cast as gels and dried in the form of rods, 1 cm in diameter by 4 cm in length. The synthesis conditions for the gels used in this study produced an aerogel with a density of 0.07 g/cm<sup>3</sup> which corresponds to a solid fraction of  $\approx 2\%$ . The chemical and structural properties of VAG monoliths were reported previously.<sup>8</sup> The aerogel materials are electronically conducting with room temperature values  $\approx 1 \times 10^{-4}$  S/cm for the composition V<sub>2</sub>O<sub>5</sub> · 0.5 H<sub>2</sub>O.

The vanadium oxide aerogels were ground into fine powders and mixed with cyclopentanone (Aldrich Chemical Co.). This mixture was stirred rigorously for 12 hours after which the VAG particles became suspended in the cyclopentanone. The VAG-cyclopentanone mixture was spun onto molybdenum coated glass slides to obtain thin films which were heat treated at 125°C for 12 hours. The films were then exposed to laboratory air and allowed to hydrate under ambient conditions.

A 1M solution of LiClO<sub>4</sub> (Aldrich Chemical Co.) in anhydrous propylene carbonate (Aldrich Chemical Co.) was prepared in an argon atmosphere glove box and used as the electrolyte. Elemental lithium served as both the counter and reference electrode, and the VAG film was used as the working electrode. Cyclic voltammetry (CV) was carried out on six thin film samples. Film thicknesses were determined from scanning electron microscopy and found to vary from 1 μm to 4 μm. The film weight was determined using a Cahn C-31 microbalance, and the

charge measurements were calculated by integration of the cathodic and anodic sweeps in the experiments.

## Results and Discussion

The open circuit potential ( $V_{oc}$ ) of the cells was approximately 3.7 V. The CV scans started at 3.6 V, decreased to 1.6 V, and then returned to 3.6 V at a sweep rate of 1mV/s. After the first sweep, the  $V_{oc}$  decreased to approximately 3.4 V. The reduction in the  $V_{oc}$  from 3.7 V to 3.4 V after the first sweep suggests that some Li was inserted irreversibly into the VAG. This amount was determined from the current-time response at a constant voltage of 3.7 V and was found to be less than 10% of the total lithium intercalated. The amount of intercalated Li ( $x$  in  $Li_xV_2O_5$ ) was calculated by integrating the anodic and cathodic sweeps and measuring the weight of aerogel in the film. The weight of the VAG included the adsorbed water; previous experiments with aerogels found that  $n$  in  $V_2O_5 \cdot n H_2O$  was between 2.0 and 2.2.<sup>8</sup> It should also be noted that the value of  $x$  assumes that all the charge is associated with lithium intercalation.

A representative CV plot for the six films is shown in Fig. 1. The sample was scanned five consecutive times and only the first and fifth sweeps are plotted. Two distinct intercalation peaks were present at approximately 2.85 V and 2.35 V, followed by a large deintercalation peak at 3.3 V. It appears that there were two peaks (2.95 V and 3.3 V) superimposed on the large deintercalation wave. The first peak at 2.95 V, however, disappeared upon further cycling. There was relatively little change in the CV plot between the first and fifth cycles. All of the peaks remained at constant potentials except for the deintercalation peak which shifted from 3.3 V to 3.5 V. The total charge for the first and fifth sweeps decreased only slightly, from 0.24 C to 0.23 C. The value of  $x$  in  $Li_xV_2O_5$  ranged from 1.2 to 1.9 for the six films tested.

The behavior shown in Figure 1 is comparable to that reported for vanadium pentoxide xerogels. The aerogel intercalation peaks are at potentials similar to those obtained with xerogel

films (2.85 V, 2.55 V and 2.33 V).<sup>4</sup> The degree of lithium intercalation is within the range reported for xerogels by some researchers<sup>2,3</sup> but less than the  $x = 3$  value reported recently.<sup>4</sup> It is important to emphasize that the morphology of the materials investigated here is significantly different from that of xerogels prepared by aqueous methods.<sup>1</sup> Not only are the aerogels highly porous (98% vs.  $\approx 50\%$ ) and have substantially greater surface area ( $400 \text{ m}^2/\text{g}$  vs.  $< 10 \text{ m}^2/\text{g}$ ), they also possess a rather different microstructure than that of xerogels.<sup>8</sup> Despite these significant morphological differences, the present results demonstrate that aerogels exhibit reversible intercalation reactions comparable to those observed with xerogels.

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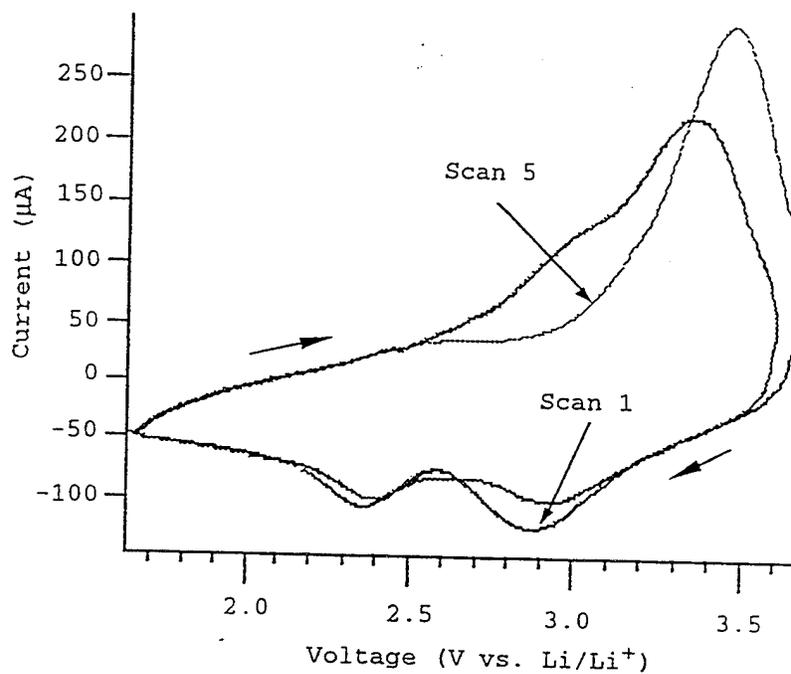


Figure 1  
First and fifth CV scans of vanadium oxide aerogel electrode in 1M solution of LiClO<sub>4</sub> in propylene carbonate. The sweep rate was 1 mV/sec. The direction of the scan is as indicated.