

## Sodium Ion Intercalation into Vanadate Films

### 1.0 Introduction

Li-Ion batteries are a mature technology for energy storage that are commonplace in electronic devices, electric power tools, and even automobiles. Sodium-based batteries are attractive alternatives for stationary energy storage applications because of lower cost and wider abundance of sodium versus lithium. In comparison to  $\text{Li}^+$ , the  $\text{Na}^+$  cation is heavier (23 g/mol vs 6.94 g/mol) and larger (0.098 nm vs 0.069 nm) leading to lower gravimetric energy and perhaps slower kinetics of insertion and release from host materials. A recent review on Na systems is available [Yabuuchi, et al. 2014]

In the search for suitable materials for Na-Ion battery electrodes and electrolytes, the mature technology of the Li-Ion technology allows one to take advantage of parallels between the two systems. The Smyrl laboratory has extensive experience with intercalation electrode materials for Li-Ion technology, and the performance of full cell systems is routinely evaluated. Full systems have been: metallic Li foil electrodes as the negative (anode), lithium perchlorate in propylene carbonate electrolytes, and  $\text{V}_2\text{O}_5$  intercalation hosts as the positive (cathode). We have more than 20 publications on various forms of  $\text{V}_2\text{O}_5$  – derived from sol-gel synthesis: solidified xerogel [Passerini, et al. 1995], solidified aerogel [Le, et al (1998)], and solidified doped aerogel. The first (xerogel) has low surface area, and the latter two materials have high surface areas (more than 300  $\text{m}^2/\text{gm}$ ). The high surface area and porous structure enable the latter materials to have high

rates of insertion and release of  $\text{Li}^+$  ions. The total capacity is (4  $\text{Li}^+$  ions/mole of  $\text{V}_2\text{O}_5$ ) and it is reversible [Le, et al. 1998].

The present research explored replacing Li with Na for Na-Ion battery systems. The cell components to be studied will be  $\text{Na}_3\text{VO}_4$  mixed with carbon for the anode, to replace Li foil. We prefer to avoid using metallic Na foil. The sodium vanadate will intercalate  $\text{Na}^+$  ions based on previous literature reports. The electrolyte will be  $\text{NaClO}_4$  in propylene carbonate. The cathode will be  $\text{V}_2\text{O}_5$  -doped with copper (Cu). The aerogel material has recently been studied as a host for  $\text{Na}^+$  ions as a negative (anode material) [Buchholz, et al. 2013], but we have demonstrated that the aerogel hosts polyvalent cations (e.g.  $\text{Mg}^{+2}$ ,  $\text{Al}^{+3}$ , and  $\text{Zn}^{+2}$ ) as a positive (cathode) material. It is expected that sodium will behave like the lithium system [Le, et al (1998)]

Cells will be assembled in the glove boxes and in the Dry Room in the Smyrl laboratory, and studied for cell cycling and capacity. We expect that 4 (moles of  $\text{Na}^+$  ion/ mole of  $\text{V}_2\text{O}_5$ ) will be inserted and released. Previous studies in the literature report successful  $\text{Na}^+$  ion intercalation in electrodeposited  $\text{V}_2\text{O}_5$  films [Tepavcevic, et al. 2012], but at lower ion capacity.

In our early literature search, it was discovered that Znaidi, et al (1989) had inserted 0.33 moles of  $\text{Na}^+$  ions into  $\text{V}_2\text{O}_5$  films in aqueous solutions by a chemical route. As a result, the interlayer spacing between bilayer  $\text{V}_2\text{O}_5$  ribbons was increased from 0.88 nm to 1.2 nm. The increased spacing is similar to that for  $\text{V}_2\text{O}_5$  aerogels that have we targeted for the current study. It is proposed that the increased spacing may make the new  $\text{Na}_{0.33}\text{V}_2\text{O}_5$  materials may be suitable hosts for

high capacity Na<sup>+</sup> ion insertion. The new material was chosen for the studies described below.

## 2.0 Experimental Procedure

Aqueous V<sub>2</sub>O<sub>5</sub> films on glass slides were manually deposited on glass slides whereupon a platinum wire-wrapped glass rod was used to control the uniform thickness of the film to 127 microns. These films were then dried in ambient air before doping with Sodium to obtain Na<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub>.

Similarly, aqueous Ketjen Black Carbon was mixed with V<sub>2</sub>O<sub>5</sub> in the ratio of 60% V<sub>2</sub>O<sub>5</sub> and 40% Ketjen Black Carbon, which was then uniformly coated on glass slides using the same glass rod and wire technique. These films were also dried in ambient and subsequently doped with Sodium to obtain 60% Na<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> 40% Ketjen Black Carbon

The current collector materials are thin Aluminum foil covered on both sides with a thin carbon film (2 microns thick). The total collector is 25 microns thick. This provides a conductive substrate on which to deposit electroactive materials for electrochemical characterization.

We studied V<sub>2</sub>O<sub>5</sub> films (127 microns thick) deposited on one side of the current collector. The film was deposited by using the Pt Wire/Glass Rod method described above. Once the film had dried in air, it was immersed in either 0.1M NaCl (Znaidi, et al 1989) or 0.1M NaClO<sub>4</sub>. The immersion did not disturb the deposited film which remained attached to the substrate current collector. The mass of the deposited V<sub>2</sub>O<sub>5</sub> film was determined with an analytical balance.

The studies also deposited composite films of 60%V<sub>2</sub>O<sub>5</sub>/40% Carbon (Ketjen Black) for comparison to the V<sub>2</sub>O<sub>5</sub> films. It was found that the Pt Wire/Glass Rod assembly did not work well for the composite film deposition. A Doctor Blade technique was used instead for the latter materials. Composite films of 120 microns were deposited on the current collector, and the mass of the assembled film was measured by an analytical balance. Films of a nominal 60 micron thickness were deposited on other samples, and the film mass was determined.

## **2.1 Preparation Techniques**

Film spreading is the first preparation technique used. This is done in two ways: a wire-wrapped glass rod and a doctor blade. The glass rod is helically wrapped with a 127 micron diameter platinum wire. An amount of V<sub>2</sub>O<sub>5</sub> is spread on one side of a glass slide or current collector, across the width of the substrate. Then, the rod-wire apparatus is used to manually spread the V<sub>2</sub>O<sub>5</sub> down the length of the substrate and subsequently pulling the excess back towards the original starting point. This process is repeatedly until full coverage of a uniform thickness is achieved.

The doctor blade is used in a similar manner. In contrast, the film material is initially placed on all parts of the substrate, after which the doctor blade is placed on top of the substrate. Then, the doctor blade can be moved horizontally back and forth in order to scrape the excess off of the substrate and achieve a uniform thickness.

Aqueous V<sub>2</sub>O<sub>5</sub> gels were used for sample preparation and characterization. The gel in the Smyrl laboratory is made as described in the seminal Livage reference

(Livage 1991). Sodium metavanadate was dissolved in deionized water to a concentration of 0.5M. The solution is then passed through an ion-exchange column to replace  $\text{Na}^+$  ions with  $\text{H}^+$  ions. This induces a sol-gel transformation. The effluent from the column is red and rapidly goes from “sol” to a “gel” state. The gel state is mature after about 1 day and does not change thereafter. The  $\text{V}_2\text{O}_5$  (red color) is stable for decades (Livage 1991). The gel is noted as 0.5M because that is the concentration of the parent solution of sodium metavanadate, and is the source for intercalation films and electrodes. When the gel is dried in air from the aqueous gel, for example as a spin coated compact film, it is a xerogel. It is amorphous with some local structure with a low surface area ( $\sim 1\text{m}^2/\text{g}$ ).

The Smyrl research group was the first to report on the synthesis of  $\text{V}_2\text{O}_5$  aerogels (Lee et al ). In the formation of the aerogel, the aqueous gel is treated with acetone to replace water in the pores. It is then treated with supercritical  $\text{CO}_2$  to replace acetone in the pores and dried in the supercritical state. Because there is no surface tension in supercritical  $\text{CO}_2$ , drying does not collapse the pores. The surface area of  $\text{V}_2\text{O}_5$  aerogel has a surface area of  $400\text{ m}^2/\text{g}$ .

Following Znaidi, et al. (1989), we formed films of  $\text{V}_2\text{O}_5$  xerogel on glass slides and on current collectors as described above. The 0.5M  $\text{V}_2\text{O}_5$  gel was used directly to form 127 micron films on glass slides. The deposited film was red (characteristic of the  $\text{V}^{+5}$  oxidation state) and corresponds to the xerogel state. After drying in ambient lab air, the film formed this way has a composition of  $\text{V}_2\text{O}_5 \bullet 1.5\text{H}_2\text{O}$  (Livage 1991). The dried film on glass slides was treated with aqueous 0.1M NaCl to insert 0.33 moles of  $\text{Na}^+$  ion to form  $\text{Na}_{0.33}\text{V}_2\text{O}_5 \bullet 1.5\text{H}_2\text{O}$ .

When treated with vacuum and temperatures of 100°C, the interstitial water is removed to produce  $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot 0.3\text{H}_2\text{O}$ .  $\text{V}_2\text{O}_5$  films on glass slides are not suitable for electrochemical studies, but the observations were helpful for further work on films deposited on a current collector substrate.

Therefore, the films were deposited as 120 micron films on the current collector.

The dried (Na doped) films were then used in electrochemical cells for  $\text{Na}^+$  ion insertion studies.

In order to facilitate  $\text{Na}^+$  ion insertion, composite films of  $\text{V}_2\text{O}_5$  (60%) and Carbon (40% Ketjen Black) were deposited by the Doctor Blade technique onto the current collector substrate. The composite films were a mixture of  $\text{V}_2\text{O}_5$  aqueous gel (0.5M) and Ketjen Black carbon particles. The mass loading of the composite film on the current collector was measured by an analytical balance.

## **2.2 Characterization**

Electrochemical characterization was performed using cyclic voltammetry and GITT. Cyclic voltammetry was used to determine the reversibility and behavior of the intercalation while GITT was used to evaluate how many ions can be inserted into the material and thus determine the ratio of sodium ions to vanadate ions in the electrode.

## **3.0 Results and Discussion**

From the cyclic voltammetry curves that resulted from the initial 127 micron  $\text{V}_2\text{O}_5$  films on 7/16" discs, it can be concluded that there are conductivity limitations present. This is found to be the case because the number of moles of  $\text{Na}^+$  per mole of  $\text{V}_2\text{O}_5$  stayed near  $\sim 0.33$ , while the literature reported more than 3 moles of  $\text{Na}^+$  per

mole of  $V_2O_5$  (Livage 1991). In contrast, when 40% carbon was used in the mixture of the thin films and the film thickness was roughly halved ( $\sim 60$  micron) the number of moles of  $Na^+$  per mole of  $V_2O_5$  increased an order of magnitude to  $\sim 3.33$  moles of  $Na^+$  per mole of  $V_2O_5$ . The conductivity issue with the thicker films could potentially be ameliorated with a longer doping time, since the 127 micron films were doped on a similar timescale as the literature 40 micron films (30 minutes) (Livage 1991).

This shows that xerogels mixtures such as the ones used in this study can be used as suitable sodium intercalation electrodes. There were some physical characteristics observed that must be addressed before these carbon- $V_2O_5$  films are ready for any sort of application. The main problem being the lack of mechanical stability at small thicknesses. After  $Na^+$  doping the subsequent drying severely damaged the structural stability of the thin ( $\sim 60$  micron) carbon- $V_2O_5$  films and led to flaking of 25-50% of the film on the current collectors. One potential solution to this problem would be the use of a binder, which is quite effective and common in areas of electrochemistry. It is notable that the 127 micron films had significantly less flaking ( $\sim 5\%$ ) due to greater mechanical stability.

#### **4.0 Conclusions**

Several conclusions can be drawn from the evaluation of  $V_2O_5$  and associated mixtures as intercalation hosts. First, the thicker films possess far greater mechanical stability but poor conductivity and sodium intercalation ability, and thus would not be suitable hosts unless further doping was evaluated. Conversely, the thin carbon- $V_2O_5$  possessed much greater conductivity and subsequent sodium

hosting abilities, with the drawback of poor mechanical stability, that could be fixed with appropriate binder mixing.

## 5.0 References

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