

Preparation and characterization of nanostructured V_2O_5 as a cathode material for Li-ion batteries

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Abstract—Nanostructured vanadium pentoxide has been widely researched as a potential candidate for cathode materials in lithium-ion batteries, due to its high theoretical capacity and superior safety characteristics. Although extensive research is available on the effect of altering preparation methods of V_2O_5 , a limited number of studies focus on the preparation conditions. In this project, the effect of changing preparation conditions on electrochemical performance was assessed. V_2O_5 samples, prepared by the polymer precursor method, were heated in either air or argon during the preparation stage. The compounds were characterised by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Galvanostatic Cycling. The samples showed distinct differences in morphology, where the sample heated in argon had larger particles and was highly impure compared to that heated in air. The compound heated in air showed better electrochemical performance by delivering a discharge capacity of 194 g^{-1} at the end of the 2nd cycle, with capacity retention of 73.7% after 50 cycles, while the compound heated in argon had a discharge capacity of 89 g^{-1} at the end of the 2nd cycle, and capacity retention of only 25.8% after 50 cycles.

I. INTRODUCTION

Lithium-ion batteries are one of the most widely-used power sources for portable electronic devices. However, commercially used cathode materials such as lithium cobalt oxide ($LiCoO_2$) and lithium iron phosphate ($LiFePO_4$) have various drawbacks; they have low energy density, pose safety hazards and are relatively more toxic in nature. This has piqued interest in other promising cathode materials. A satisfactory battery should have high specific energy, low cost production, a longer life span and should be safe to use. In this project, vanadium pentoxide (V_2O_5) was chosen for its high theoretical capacity (294 mAh/g) as compared to $LiCoO_2$ (140 mAh/g) or $LiFePO_4$ (170mAh/g). V_2O_5 also offers the advantage of low cost and superior safety characteristics during overcharging due to the multiple oxidation states of the vanadium atom [1]. Though a battery with V_2O_5 has poor cycle life, the need for better power sources to supplement an increasing energy demand prompts research in V_2O_5 as a cathode material.

The preparation method and conditions of the nanostructured V_2O_5 determines its purity and crystal structure, which greatly influences the electrochemical performance of the battery. Extensive research has been done

to compare the effect of preparation methods on electrochemical performance of the batteries [2] [3] [4]. Compared to other methods such as the hydrogen peroxide and surfactant method, V_2O_5 nanocrystals prepared by the polymer precursor method have shown favorable characteristics [1]. However, limited research is available on the effect of altering the preparation conditions of the aforementioned method, namely, the environment that the reactants are heated in to produce the V_2O_5 powder. This largely alters the particle size and structure of the compound formed, thus it is an essential area of study.

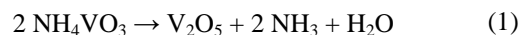
Rhodes et al. [5] found that V_2O_5 gels synthesized by the sol-gel process showed better electrochemical performance when heated in air during the preparation stage compared to when heated in an inert atmosphere. However, an inert atmosphere improves purity of the compound formed by preventing any side reactions from taking place.

In this project, the polymer precursor method was used to synthesize the V_2O_5 nanocrystals. This method was preferred due to its simplicity [6] and convenience of bulk preparation. The effect of altering the preparation conditions of V_2O_5 on the electrochemical performance of a lithium-ion battery was studied. V_2O_5 samples were prepared either by heating in air or in argon.

II. METHODOLOGY

A. Preparation of Materials

V_2O_5 was prepared using the PVP precursor method. 3 grams of Ammonium Metavanadate (NH_4VO_3) (Merck, purity 99%) was mixed with 5 grams of the polymer PVP (polyvinylpyrrolidone) (Aldrich 99%), then ground up and heated in a furnace for 3 hours at 450°C . Equation (1) shows how the thermal decomposition of Ammonium Metavanadate takes place to obtain V_2O_5 .



One sample was heated in a box furnace in air and the other sample was heated in a tube furnace in argon. The samples were named $V_2O_5\text{-O}$ (O-oxygen) and $V_2O_5\text{-A}$

(A-argon) respectively. The V_2O_5 -O and V_2O_5 -A produced were yellow and black respectively.

B. Electrode Fabrication

The electrodes were fabricated with the active material V_2O_5 . The V_2O_5 powder, PVDF (polyvinylidene fluoride) binder and conductive agent Super P Carbon were mixed in a weight ratio of 70: 15: 15, with NMP (*N*-methyl-2-pyrrolidone) as a solvent. The resulting slurry was left in a magnetic stirrer overnight. It was coated on an aluminium foil current collector (this foil is stable up to 5.0V), using the doctor blade technique to ensure uniformity of coating (thickness 1mm), then pressed between twin rollers and dried in the oven. Aluminium foil was used since it does not take part in the undergoing reactions in the cell. Circular electrodes were punched and dried under vacuum at 70 °C for 8 hours.

C. Battery Fabrication

The coin cells were fabricated in an argon-filled glove box, using Li-metal foil as counter and reference electrodes, and 1M $LiPF_6$ solution as electrolyte. The assembled cell was pressed with a coin-cell press. A voltage of at least 2.5V for all cells while measuring the open-circuit voltage (OCV) indicated the cells could be used for further testing. The cells were subject to galvanostatic charge-discharge tests using a Battery Life- cycle Tester (Bitrode, USA). X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) were used to characterise the compounds prepared.

III. RESULTS AND DISCUSSION

A. Structure and Morphology – Scanning Electron Microscope

The Scanning Electron Microscope (SEM) images of V_2O_5 -O and V_2O_5 -A are shown in Fig. 1a and 1b respectively.

There is a clear distinction in particle size observed, where V_2O_5 -O particles are much smaller in size than V_2O_5 -A particles. However, V_2O_5 -O particles formed large chunks with low exposed surface area while V_2O_5 -A particles formed smaller agglomerates with a larger surface area. Permeability is expected to be higher in V_2O_5 -A particles, due to the presence of pockets between particles for lithium intercalation. However, this could also prevent deintercalation by trapping the lithium ions inside the structure.

B. Structure and Morphology – X-Ray Diffraction

X-Ray Diffraction (XRD) was carried out to ensure purity of the compound produced. Fig. 2a and 2b show the XRD patterns obtained for V_2O_5 -O and V_2O_5 -A respectively.

The asymmetry of the peak patterns shows orthorhombic structures for both compounds. Lattice parameter values for V_2O_5 -O are $a = 11.510 \text{ \AA}$, $b = 4.373 \text{ \AA}$, $c = 3.563 \text{ \AA}$, while that for V_2O_5 -A are $a = 10.004 \text{ \AA}$, $b = 5.040 \text{ \AA}$, $c = 9.854 \text{ \AA}$. The values for V_2O_5 -O align closely with other experimental data on nanostructured V_2O_5 , while that of V_2O_5 -A do not.

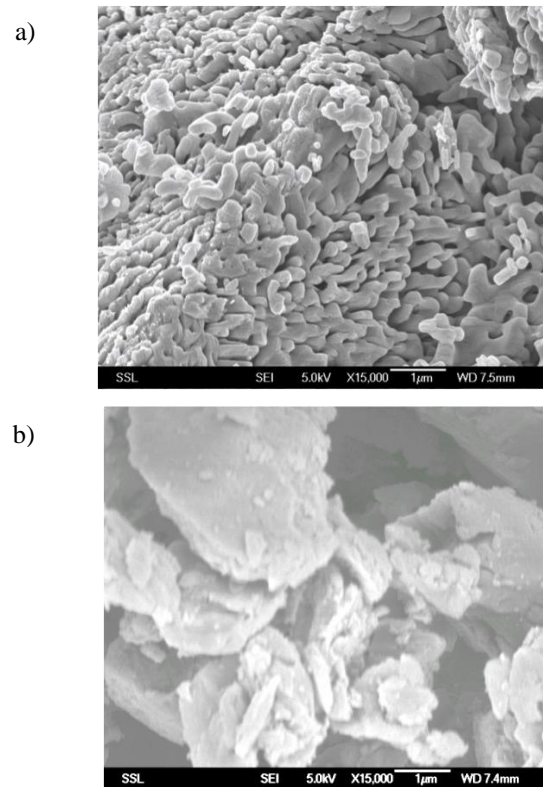


Figure 1. Scanning Electron Microscope images of V_2O_5 , prepared under 15k magnification and bar scale shown of 1 μm (a) V_2O_5 -O (b) V_2O_5 -A

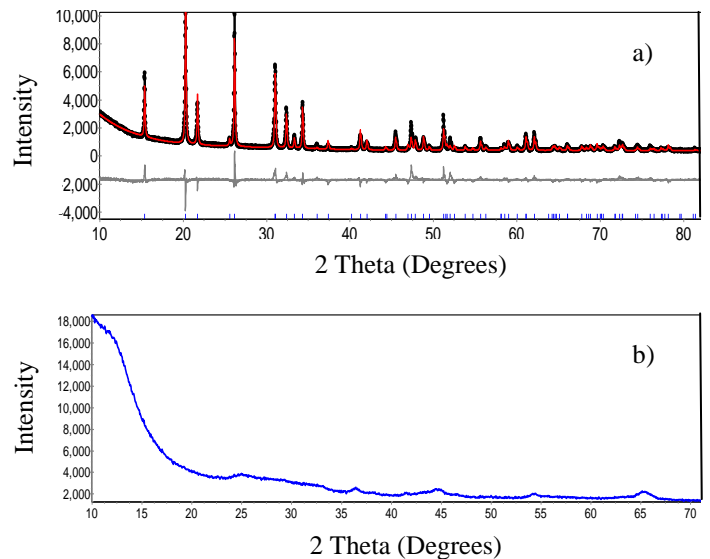


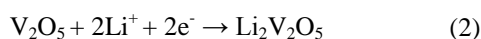
Figure 2. Powder X-Ray Diffraction patterns of (a) V_2O_5 -O, Red line: fitted data, black line: experimental data, difference pattern is at centre, (b) V_2O_5 -A. Samples were run for 40 minutes.

The peaks in Fig. 2a align closely with the peaks from reference patterns, as shown by the black line, indicating the purity of the sample. The reference patterns were obtained from a database of reported lattice parameter values. The absence of peaks in Fig. 2b shows that the compound obtained was not pure V_2O_5 . Compared to the crystalline phase of V_2O_5 -O seen by the sharp peaks in Fig. 2a, the broad peaks in

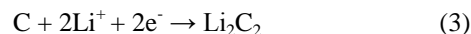
the XRD pattern of V_2O_5 -A (Fig. 2b) are representative of an amorphous phase of the compound. As this sample was heated in argon gas, it is suggested that amorphous VO_2 or amorphous V_xO_y /carbon composite phases were formed (where oxidation state of vanadium is lower than +5). Absence of oxygen during this process could have contributed to defects in the structure which leads to the formation of V_xO_y phases. This is further confirmed by the lattice parameter values that do not align with other experimental data on V_2O_5 .

C. Electrochemical Characteristics – Galvanostatic Cycling

Galvanostatic cycling was done to analyze the capacity and coulombic efficiency of the cells. Cells were charged and discharged at a constant current rate of 120mAh/g. In this case, a voltage range of 2.0-4.0V was used for a set number of cycles. Discharge-charge cycling profiles are shown in Fig. 3a. The electrochemical mechanisms of pure V_2O_5 (Fig. 3a) during the discharge cycle can be written as shown in (2).



Li is intercalated into the V_2O_5 crystals. During the charge cycle, the Lithium ions flow back from the V_2O_5 crystals to the anode. Equation (3) gives the balanced equation for the charge cycle at the anode.



The charge and discharge curves in Fig. 3a show the voltage plateaus reflecting the structural phase transformation occurring during the lithiation process, where vanadium is reduced from an oxidation state of +5 to +3 in stages. The plateaus are not visible in the discharge curves from the 10th cycle onwards in Fig. 3a. The plateaus are absent in all cycles in Fig. 3b, however, indicating structural modifications during the phase transformations of the compound formed, and thus poor Li intercalation. As V_2O_5 -A is likely to be amorphous VO_2 or V_xO_y compound, vanadium in V_2O_5 -A was not initially in the +5 oxidation state. Since the initial phase change of vanadium from an oxidation state of +5 cannot take place, Li-insertion is no longer possible for V_2O_5 -A.

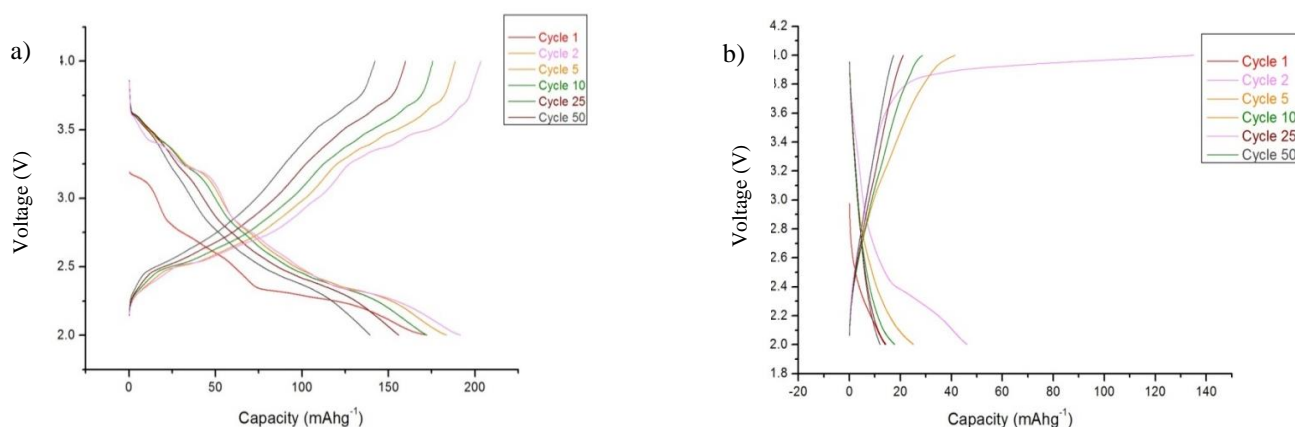


Figure 3. Galvanostatic cycling graph for (a) V_2O_5 -O (b) V_2O_5 -A [selected cycles – 1, 2, 5, 10, 25, 50] Voltage range: 2.0-4.0V, current rate 120mAh/g

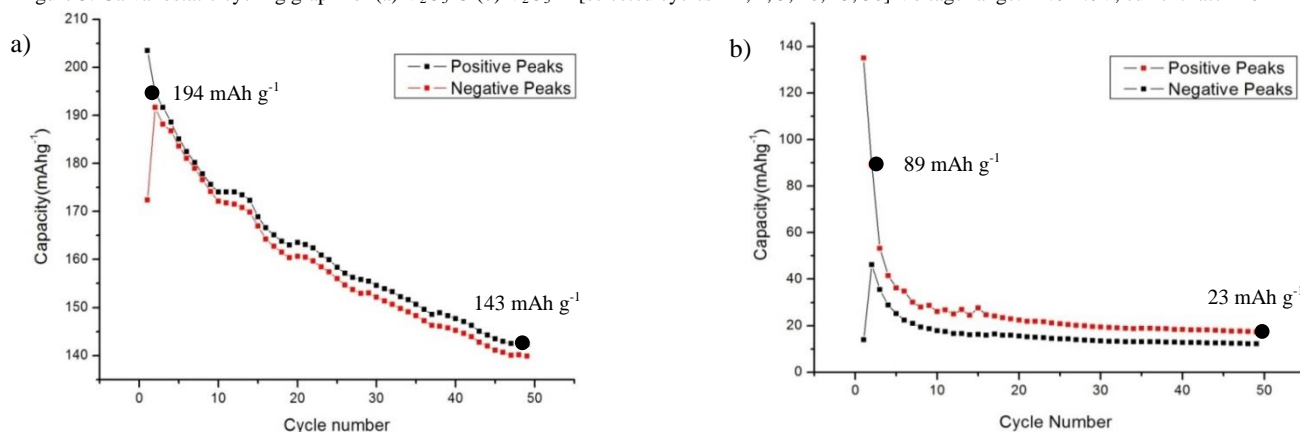


Figure 4. Capacity vs. cycle no. plots of a) V_2O_5 -O b) V_2O_5 -A, Voltage range: 2.0-4.0V, current rate 120mAh/g

The capacity vs. cycle number graphs of V_2O_5 -O and V_2O_5 -A were plotted to analyze the capacity retention and stability of the cells. Cycling data is shown in Fig. 4a and 4b.

Comparing the graphs in Fig. 4, V_2O_5 -O had significantly better capacity retention than V_2O_5 -A. The capacity of V_2O_5 -O reduced from 194 mAh g^{-1} initially to 143 mAh g^{-1} in the 50th cycle, indicating capacity retention of 73.7%. V_2O_5 -A had a charge capacity of 89 mAh g^{-1} in the first cycle, however due to capacity fading, the charge capacity was reduced to 23 mAh g^{-1} in the 50th cycle, which is a 74.2% loss of charge capacity. The life span of both samples fell below the threshold of 300-500 charge-discharge cycles in commercial lithium-ion batteries. Fig. 4a shows a gradual drop in capacity, with relatively good stability, while Fig. 4b shows a steep drop in capacity between the first and fifth cycles. The rapid capacity fading of V_2O_5 -A indicates that the efficiency of the cell reduces quickly and is not suitable to be used commercially, particularly given that a typical lithium ion battery system retains less than 50% of its capacity only after 100 cycles. Based on the SEM images of V_2O_5 -A, the presence of pockets in between particles could prevent deintercalation from taking place by trapping lithium ions inside the structure. This could potentially hamper the working of the cell, reducing its capacity at a much faster rate. A more detailed analysis of the sample is required to pinpoint the cause of this drop.

IV. DISCUSSION

It is to be noted that the maximum capacity obtained for both compounds was lower than expected and fell far below the theoretical capacity of V_2O_5 , which is 294 mAh g^{-1} . This could be attributed to the amorphous V_xO_y phases formed in V_2O_5 -A after heating in an inert atmosphere. Reference [5] suggested that heating in argon decreases the relative distribution of intercalation sites related to V_2O_5 . Therefore, heating in an excess of oxygen would ensure that pure V_2O_5 is formed. It is uncertain whether heating in a pure oxygen environment would then improve the performance of V_2O_5 . To test this hypothesis, a V_2O_5 sample could be prepared by heating in pure oxygen and its performance would have to be compared to a sample heated in air. The lower than expected capacity of V_2O_5 -O could have been due to the agglomeration of the particles into large chunks, as seen by the SEM images, thus decreasing permeability. As V_2O_5 is shown to be highly sensitive to small changes in preparation, more research has to be carried out to improve the efficiency of the cells such that V_2O_5 can be viable for commercial use.

In further extensions of the project, a different method of preparation can be used in place of the polymer precursor method. In one experiment, a capacity of 270 mAh g^{-1} for facile synthesized V_2O_5 was obtained [7]; however, this method of synthesis is tedious and not favorable for industrial application. Therefore, more research has to be carried out on increasing the capacity of V_2O_5 crystals prepared by the polymer precursor method.

V. CONCLUSION

The effect of changing the preparation conditions on the V_2O_5 compounds, synthesized by the polymer precursor method, was studied. The compounds were characterized by SEM, X-ray Diffraction and Galvanostatic Cycling. There were distinct differences in the morphology of both compounds. SEM images showed that V_2O_5 -O had smaller-sized particles which had agglomerated into large chunks, while V_2O_5 -A had larger particles that had agglomerated into smaller groups. XRD data revealed that the V_2O_5 -A sample was highly impure, and its XRD graph had no defined peaks, indicating the presence of an amorphous phase. V_2O_5 -O was found to give capacity retention of 73.7%, which was significantly higher than V_2O_5 -A. V_2O_5 -O showed better stability and higher capacity in the first cycle (194 mAh g^{-1}) than V_2O_5 -A (89 mAh g^{-1}). Therefore, V_2O_5 -O, prepared by heating in air, displayed significantly better electrochemical performance than V_2O_5 -A, heated in argon.

ACKNOWLEDGMENT

I would like to thank Dr. M.V. Reddy and the staff from the Department of Physics, NUS for their constant guidance in the project, and Mr Chang Siang Wen from Victoria Junior College for his active support. I would also like to thank the faculty of science, NUS for their contribution to the project. Dr. M.V. Reddy wishes to thank National Research Foundation, Prime Minister's Office, Singapore under its Competitive Research Programme (CRP Award No. NRF-CRP 10-2012-6) for research support.

REFERENCES

- [1] Sakunthala, A.; Reddy, M. V.; Selvasekarapandian, S.; Chowdari, B. V. R.; Selvin, P. C., Energy storage studies of bare and doped vanadium pentoxide, (V_{1.95}M_{0.05})O₅, M = Nb, Ta, for lithium ion batteries. *Energy & Environmental Science* 2011, 4, (5), 1712-1725.
- [2] Yin, D.; Xu, N.; Zhang, J.; Zheng, X., High quality vanadium dioxide films prepared by an inorganic sol-gel method. *Materials Research Bulletin* 1996, 31, (3), 335-340.
- [3] Sudant, G.; Baudrin, E.; Dunn, B.; Tarascon, J., Synthesis and Electrochemical Properties of Vanadium Oxide Aerogels Prepared by a Freeze-Drying Process. *Journal of The Electrochemical Society* 2004, 151, (5), 13-4651.
- [4] Mohan, V. M.; Hu, B.; Qiu, W.; Chen, W., Synthesis, structural, and electrochemical performance of V₂O₅ nanotubes as cathode material for lithium battery. *Journal of Applied Electrochemistry* 2009, 39, 2001-2006.
- [5] Rhodes, C. P.; Dong, W.; Long, J. W.; Rolison, D. R., Controlling defects in nanostructured V₂O₅: Spectroelectrochemical characterization. *Solid-state Ionic Devices III* 2002, 3, (26), 478-489.
- [6] Lazarevic, Z. Z.; Romcevic, N. Z.; Stojanovic, B. D., Synthesis and characterization of barium strontium titanate powder. *Journal of Optoelectronics and Advanced Materials* 2008, 10, (10), 2675-2677.
- [7] Pan, A.; Zhang, J. G.; Nie, Z.; Cao, G.; Arey, B. W.; Li, G.; Liang, S. G.; Liu, J., Facile synthesized nanorod structured vanadium pentoxide for high-rate lithium batteries. *Journal of Materials Chemistry* 2010, 20, 9193-9199.
- [8] Su, D.S.; Schlögl, R., Thermal decomposition of divanadium pentoxide V₂O₅: Towards a nanocrystalline V₂O₃ phase. *Catalysis Letters* 2002, 83, (3-4), 115-119.

- [9] Ban, C., Synthesis and characterization of nano-scale vanadium oxides, vanadium phosphates as cathodes for lithium batteries. ProQuest 2008.
- [10] Bystrom, A.; Wilhelmi, K. A.; Brotzan, O., Acta Chemica Scandinavia, 4, (1950), 1119.
- [11] Perlstein, J. H.; J. Solid State Chem., 3, (1971), 217.
- [12] Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M., Nano-sized transition-metaloxides as negative-electrode materials for lithium-ion batteries. Nature 2000, 407, (6803), 496-499.
- [13] Reddy, M. V.; Subba Rao, G. V.; Chowdari, B. V. R., Metal oxides and oxy salts as a anode materials for Lithium batteries. Chem. Rev. 113 (2012) 5364-5457.
- [14] Chernova, N. A.; Roppolo, M.; Dillon, A. C.; Whittingham, M. S., Layered vanadium and molybdenum oxides: batteries and electrochromics. J. Mater. Chem. 2009, 19, (17), 2526-2552.
- [15] Zaban, A.; Zinigrad, E.; Aurbach, D., Impedance spectroscopy of Li electrodes .4. A general simple model of the Li-solution interphase in polar aprotic systems. J. Phys. Chem. 1996, 100, (8), 3089-3101.
- [16] A. Moretti, et al., V2O5 electrodes with extended cycling ability and improved rate performance using polyacrylic acid as binder. Journal of Power Sources 2014, 09, (150), 0378-7753.