Summary of the Performance of V$_2$O$_5$ Materials as Lithium Battery Cathode

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Abstract: Lithium battery has recently gained more and more attention worldwide. It has wide usage that range from toys to electric cars. Choosing a suitable material that best fits the overall performance as electrode for the battery is very essential. For cathode material, apart from the traditional and widely-used LiCoO$_2$, LiFePO$_4$ and so on, there are innovations that include the use of V$_2$O$_5$. Researches have been done focusing on how to further improve the performance for V$_2$O$_5$ cathode in terms of different structure, forms or combination with other chemical molecules. This research paper will make a summary of the materials derived from traditional V$_2$O$_5$ as well as their performances.

Keywords: Lithium battery; Cathode material; V$_2$O$_5$ materials and performance

Publication date: July 2021; Online publication: July 31, 2021

1. Introduction

The development of high-performance lithium ion batteries is mainly limited by the relatively low capacity of the negative electrode and poor cycling stability. Considering the limitations of LiCoO$_2$, LiMn$_2$O$_4$ and other traditional cathode materials, the low theoretical capacity and multi-step synthesis requirements of LiFePO$_4$, these materials do not have advantages for flexible wearable electronic devices in the new era [1-2]. However, a new type of cathode material V$_2$O$_5$ with high theoretical specific capacity and abundant activity in nature appears to be a very appealing choice. V$_2$O$_5$ has a variety of derived materials which make it has a great research prospect. Vanadium-based compounds exhibit a range of oxidation states, including V$^{5+}$, V$^{4+}$, V$^{3+}$, and V$^{2+}$, making them feasible to composite with many other anions and cations to form vanadium oxides [3].

Poor cyclic performance is the most important problem for V$_2$O$_5$ materials and its derivatives. The most serious problem for traditional lithium battery cathode materials is that the long cycle stability, good rate capability, and high mass loading cannot be achieved at the same time [4], which is caused by the irreversible Li$^+$ intercalation at the deep discharge condition.

In this passage, several different materials derived and improved from the original vanadium oxides compound in terms of their performance are concluded. These materials include V$_2$O$_5$ with HoMSs, O vacancies and so on, while also in different forms, such as in xerogel forms and in nanotube form. Many of them have significant improvement compared with traditional form considering in charge-discharge capacity and other means, but meanwhile perform poorer in other aspects, especially in the performance of stable cyclability.
2. Materials and Performances
2.1. V2O5 Nanotubes

V2O5 nanotube array has initial capacity of 300 mA h g⁻¹, which is almost two times higher compared to the initial capacity of the traditional V2O5 film, which is 140 mA h g⁻¹. Short diffusion distance and large surface area of the nanotube array are the main reasons for this improvement in capacity.

However, unstable discharge cyclability performance is still obvious (the capacity is reduced to 2001 and 180 mA h g⁻¹ at the second and third charge and discharge), but there is still improvement compared with colloidal or ordinary V2O5 film (30% more power than traditional V2O5 film at the sixth charge and discharge) [5-6].

Newly reported improvement related to V2O5 Nanofibers includes V2O5/CNT (Carbon nanotube). Figure 2. shows the number of cycles in the relation with capacitance retention. V2O5/CNTs composites have good electrochemical stability, and after 5000 cycles, the capacitance loss is only 8.8%, which is a high result compared with other electrodes.

It was found that V2O5 /CNTs with weight ratio 0.5:1 had the highest capacitance among different ratios. Due to mutual penetration of carbon nanotubes and V2O5 nanosheets, the composite structure is layered porous. Based on the structure of V2O5, the conductivity of CNTs and the high capacity of V2O5,
V2O5/CNT electrode has a power density (0.27 W cm−3) and energy density (1.47 mWh cm−3) [7].

2.2. V2O5 HoMSs (3D hollow multi-shelled structures)

The HoMSs, also known as 3D hollow multi-shelled structures, has more active sites and more surface-volume ratio can be provided for lithium-ion storage to improve the specific capacity of cathode. In addition, due to the shorter path needed to transport lithium electrons and ions and increased electrode-electrolyte contact area, HoMSs can make lithium ions enter lithium ions better, thus improving the rate capacity.

A 3D textile-based cathode electrode coupling a V2O5-HoMSs active material with a metal fabric collector for good quality flexible lithium batteries has been reported by Zhu et al., [8]. The cathode electrode of the fabric is composed of single or multi-shell V2O5 HoMSs synthesized by STA (denoted as nS-V2O5. The number n representing number of shells) for the active material, and cotton coated by nickel (reduced to Ni-Cotton) fabric for the use of mechanical support and conductive collector. Due to the advantages of the above HoMSs, the large surface area and flexibility shown of the Ni-Cotton structure, as well as the good combination of V2O5 HoMSs and Ni-Cotton, the 3S-V2O5 HoMSs/ Ni-Cotton electrode under the high-quality load of 2.5 mg cm−2, it can maintain an astonishing capacity of 222.4 mA h g−1 even after 500 charge and discharge cycles. This proved that it has good ability for repeated use, also solving the traditional problem of cathode material in terms of poor cyclability.

As shown in Figure 3, specific discharge capacity of 3S-V2O5 HoMSs electrode was 601.8 mAh g−1 under current density of 100 mA g−1. That is much better compared with other traditional cathode material. Even when the current density increased to 1000 mA g−1, there is still a high capacity of 264.6 mA h g−1.

In Figure 3, b, the capacities of HoMSs and nanosheets after 200 cycles were respectively 268.3, 226.7, 204.0 and 173.9 mAh g−1. Maximum specific capacity electrode is obtained using the 3S-V2O5 HoMSs/Ni-cotton electrode. This is attributed to the fact that a larger surface area can be provided by 3S-V2O5 HoMSs and more active sites for lithium-ion storage, so specific capacity can be improved. Also, when compared with V2O5 nanosheets, HoMSs materials shown better cyclic stability and capacity, that is mainly due to some of the factors. Firstly, because of the pore structure, electrolyte permeates the inner shell better. Secondly, the thin shell reduces the stress caused by volume expansion and reduction, while also shortens the time needed for transportation. Thirdly, multi-shell structures may provide more places to store lithium.

Figure 3. Note that V2O5 Hollow sphere also known as 1S-V2O5
2.3. Orthorhombic phase V\textsubscript{2}O\textsubscript{5} with O vacancies (denoted as V- V\textsubscript{2}O\textsubscript{5})

V-V\textsubscript{2}O\textsubscript{5} is also an appealing material available for use in lithium battery cathode. Figure 4. are SEM, TEM images showing pure V\textsubscript{2}O\textsubscript{5} and V- V\textsubscript{2}O\textsubscript{5}. From the graph provided, it is clear that both V-V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{5} have two-dimensional lamellar morphology. Using higher magnification SEM and TEM images, V-V\textsubscript{2}O\textsubscript{5} has many deeper troughs on the surface and large surface fluctuations (Figure 4. c, g, h), whereas V\textsubscript{2}O\textsubscript{5} is a slab fracture attributable to mechanical forces during sample preparation (Figure 4. f, j, k), the rough surface of V- V\textsubscript{2}O\textsubscript{5} more effectively inhibits the accumulation of flakes, stores more electrolytes, provides more material-electrolyte contact area, and loosens mechanical strain resulting from insertion/disinsertion cycle of Li\textsuperscript{+} compared with pure V\textsubscript{2}O\textsubscript{5}[9].

Figure 4. SEM, TEM samples of V\textsubscript{2}O\textsubscript{5} and V-V\textsubscript{2}O\textsubscript{5}[9]

According to Sun et al., at the current density of 200 mA g\textsuperscript{-1}, Figure 5. a shows the cyclic ability for both the V-V\textsubscript{2}O\textsubscript{5} and the pure V\textsubscript{2}O\textsubscript{5} electrode. Compared with pure V\textsubscript{2}O\textsubscript{5}, it is clear that V-V\textsubscript{2}O\textsubscript{5} shows better discharge capacity. Given current density of 1A g\textsuperscript{-1} (Figure 5. c), maximum specific discharge capacity of V-V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{5} is respectively 230.2 and 256.6 mAh g\textsuperscript{-1}. The discharge capacity after 50 cycles are respectively 213.1 and 237.9 mAh g\textsuperscript{-1}, and the discharge capacity after 100 cycles are respectively 199.2 and 224.7 mAh g\textsuperscript{-1}. Insertion/ removal capacity of Lithium ions in V- V\textsubscript{2}O\textsubscript{5} are always better compared with traditional V\textsubscript{2}O\textsubscript{5}. The capacity retention rate of V-V\textsubscript{2}O\textsubscript{5} still remains at 87.6% at the 100th cycle. Even at higher current density of 3A g\textsuperscript{-1}, as shown in Figure 5. d, excellent discharge capacity stability is still shown on the graph, always higher than that of V\textsubscript{2}O\textsubscript{5}, and remain at the value for approximately 150 mAh g\textsuperscript{-1} for all the cycle number smaller than 200.

Cyclic stability of V\textsubscript{2}O\textsubscript{5} and V-V\textsubscript{2}O\textsubscript{5} samples is compared for 1 and 3 g\textsuperscript{-1} current density (Figure 5. c, d). At 1A g\textsuperscript{-1}, there is first increased and then decreased discharge capacity of V-V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{5}, the maximum capacity are found to be 218.4 and 200.6 mAh g\textsuperscript{-1}. During cycle measurement, the significant increase in capacity during the first few cycles can be attributed to electrode activation (electrolyte penetration and/or active surface increase). After 200 cycles, discharge capacities of V- V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{5} are respectively to be 189.3 and 172.4 mA h\textsuperscript{-1}. When 3A g\textsuperscript{-1} is adopted, the capacity first increased slowly and remained stable for both two electrodes. Maximum discharge capacities of V\textsubscript{2}O\textsubscript{5} and V-V\textsubscript{2}O\textsubscript{5} are respectively 141.7 and 150 mAh g\textsuperscript{-1}. In the condition of hypoxia, V\textsubscript{2}O\textsubscript{5} is easy to lose the O atom in crystal structure and form Oxygen vacancy. O vacancies acts as important role to help to reduce V\textsuperscript{5+} to V\textsuperscript{4+}, improve electron and ionic conductivity, also providing additional sites for lithium ions to embed in [10-11].
Figure 5. (a) V- V₂O₅ and V₂O₅ electrodes at a current density of 200 mA g⁻¹, measured for the cyclic performance; (b) At a current density of 200 mA g⁻¹, differential specific capacity plots of the V- V₂O₅ drawn with different cycle numbers, cyclic performance of V-V₂O₅ and V₂O₅, respectively, are drawn at a current density of (c) 1 A g⁻¹ and (d) 3 A g⁻¹.

2.4. Li₂O-V₂O₅-SiO₂-B₂O₃ glass

Suitable cathode materials also include glass materials because of their controllable capacity by controlling the composition of the glass. In addition, glass materials ordered with short-range structure can have much improved dynamics, and facilitate electrochemical cycling.

SiO₂ has a very high melting point (1650±50°C), so for the Li₂O-V₂O₅-SiO₂ glass system, there is also a higher melting point. Therefore, a low melting point (450°C) B₂O₃ glass molding agent was used to reduce the melting point. In addition, because of phase separation, borosilicate glass has high ionic conductivity, and B₂O₃ can also reduce the tendency of crystallization in terms of the glass material.

In Figure 6, 20Li₂O-30V₂O₅-(50-x)SiO₂-xB₂O₃ (x=10, 20, 30, 40) are named as LVSB10, LVSB20, LVSB30 and LVSB40 sample, respectively. The two graphs provide evidence for the cyclic stability for these cathode materials. Figure 6. a and b shows the relationship between voltage and discharge capacity. Under both circumstances, 50 mAh g⁻¹ density is adopted. It is find that under the 1.5V to 4.2V voltage range, four samples display poor capacity of charging. The discharge capacities of LVSB10, LVSB20, LVSB30 and LVSB40 were 123.7 mAh g⁻¹, 51.5 mAh g⁻¹, 37.9 mAh g⁻¹ and 19.5 mAh g⁻¹, respectively.
With high V⁴⁺ ratio, in the LVSB10 sample, it has higher initial discharge capacity compared with that in other samples. Plus, the more number of V⁴⁺, the smaller polaron jump can be generally shown, thus achieving higher conductivity [12].

However, the capacity of the glass cathode material decreases rapidly. The capacities of all four LVSB materials undergo rapid decrease after 50 cycles. The capacity retention rates were hardly above 50%, showing not stable cyclability when more charge and recharge cycles are being repeated. In Figure 6, b, the results shows that LVSB glass has electrochemical activity, but poor cycling performance for glass cathode material, mainly caused by the low electron conductivity due to the large particle size and its volume may also have changed during the ion and electron extraction or insertion.

**Figure 6.** Charge and discharge curves for (a) 1st cycle, (b) 50th cycle using LVSB10, LVSB20, LVSB30 and LVSB40 as glass samples [12].

**Figure 7.** Cycle number versus discharge capacity of LVSB and LVSB-b for both fixed current density(a) and changing ones (b)

LVSB10-b can be made by milling the LVSB 10 sample, which this process can make LVSB 10 particle smaller, creating LVSB10-b with smaller particle. Cyclability ability of both LVSB and LVSB 10-b are first going to pass through a stable voltage, which ranges from 1.5V to 4.2V to give stable current density of 50 mA g⁻¹. In this case, it can be shown from Figure 7, a that LVSB 10-b obviously win in every cycle number under 100 in terms of discharge capacity. For the 100th cycle, LVSB 10-b still reaches discharge capacity of approximately 100 mAh g⁻¹, still maintain the capacity retention of nearly 70%, while the value for LVSB of discharge capacity at 100th cycle is only approximately 30 mAh g⁻¹. In Figure 7, b, providing the changing current density, LVSB 10-b still shows better performance under the condition of different current density. The main increase in cyclability is mainly due to the impedance of charge transfer.
is largely decreased, and lithium ion diffusion is rather easier. It is conjectured that due to the decrease in particle size for LVSB 10-b, both electron and lithium ion transporting pathways can be shortened, so the conductivity of the cathode can be effectively improved.

2.5. V$_2$O$_5$ xerogel

V$_2$O$_5$ xerogel can be directly made from traditional V$_2$O$_5$ crystals. The xerogel is obtained by adding molten vanadium oxide that is heated to 800°C into water. According to Huguenin et al., \cite{13} the electrochemical performance analysis showed that V$_2$O$_5$ xerogel was a suited lithium battery cathode material choice, with a reduction potential 3 higher than that of lithium, an energy density of about 600 Wh kg$^{-1}$, and a specific capacity of about 250 Ah kg$^{-1}$. However, the poor cyclability that decreases obviously with the increase of the number of cycles for vanadium oxide xerogel still exists.

<table>
<thead>
<tr>
<th>film</th>
<th>annealing gas</th>
<th>interlayer spacing (Å)</th>
<th>grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 h air</td>
<td>11.0</td>
<td>14.3</td>
</tr>
<tr>
<td>2</td>
<td>0.5 h air + 2.5 h N$_2$</td>
<td>11.1</td>
<td>11.6</td>
</tr>
<tr>
<td>3</td>
<td>2.5 h N$_2$ + 0.5 h air</td>
<td>11.2</td>
<td>6.4</td>
</tr>
<tr>
<td>4</td>
<td>3 h N$_2$</td>
<td>11.5</td>
<td>5.1</td>
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**Figure 8.** Different composition of V$_2$O$_5$ films, which are annealed with varying N$_2$ and air composition. Presence of V$^{5+}$ (yellow) and V$^{4+}$ (green) can also be known from the graph \cite{13}

Four films can be derived from the vanadium oxide xerogel in terms of different composition, as shown in Figure 8, on the left. These four films have different grain sizes and also have different chemical properties. Reduction is induced by N annealing, causing yellow V$^{5+}$ ions to green V$^{4+}$ ion. As shown in the graph, in film 1, there is no or very little V$^{4+}$; in film 2, V$^{4+}$ ions (green exterior) covers the surface of the film. There is many V$^{4+}$ ions inside the film 3 (green), but due to re-exposure to air, V$^{4+}$ on the surface of the film is oxidized to V$^{5+}$. There are V$^{4+}$ ions in film 4 as in film 3, but because only N$_2$ annealing is
applied, there is no V⁴⁺ reoxidation on the surface [13].

**Figure 9.** Films 2 and film 3 under 600 mA g⁻¹ current density of V₂O₅ at (a) 1ˢᵗ (b) 30ᵗʰ cycles for air and N₂ condition at 300 degrees Celsius for 3 hours (0.6V to 1.4V) [13]

**Figure 9.** is the graph that shows at the constant current density for 600mA g⁻¹, the voltage-capacity relationship for the first and 30ᵗʰ CP curves. In Figure 9a, the initial CP curves of film 2 and film 3 start at ~ -0.07 V and ~ 0.03 V, respectively. Compared with air-annealed films, the charge-discharge curves of both films are inclined and have clearer platform. Because of the intercalation mechanism of the solution, film 2 with low crystallinity has the discharge capacity of 139 and 137 mAh g⁻¹, and that of film 3 is respectively 129 and 133 mAh g⁻¹. However, what is appealing is that film 2 actually shows very small irreversible capacity for only 2mAh g⁻¹. This proved film 2 to have very good reversibility. In Figure 9b, for the 30ᵗʰ cycle, film 2 also displays very small irreversibility for only 1mAh g⁻¹, while that of film 3 reaches 8mAh g⁻¹. Using these data, we can conclude that in contrast with film 3, which degrades its capacity seriously within 30 cycles, film 2 shows very good coulomb efficiency with little irreversible capacity, and also better discharge capacity.

**Figure 10.** Discharge capacity versus cycle number for all the 4 films, with same condition applied in Figure 9. [13]

**Figure 10.** The discharge capacity versus cycle number graph is drawn in order to show the four film’s stability in discharge capacity maintenance. Under the condition of 600mA g⁻¹ current density condition for 50 cycle numbers, film 2 in the four lithium ion intercalated films displays best cyclic stability.
With an initial around 140 mAh g\(^{-1}\), capacity, its capacity slightly improved in the following several cycles, and reach a maximum discharge capacity for cycle number 15, and then followed by a mild decline after 15 cycles. At cycle number 15, the capacity still remains high at 136 mAh g\(^{-1}\), which shows very high coulomb efficiency for approximately 98 percent. Film 4 also display similar cyclability properties. Discharge capacity rise relatively fast with cycle number at first, with initial value about 68 mAh g\(^{-1}\). Although a slightly decline follows after around 24 cycles, final discharge capacity after 50 cycles still reaches 148 mAh g\(^{-1}\). Film 3 shows good initial discharge capacity, but it decreases fast and after 50 cycles it only reaches 75 mAh g\(^{-1}\), which is quite low with maintenance of about 60% of initial value. Capacity degradation of film 1 is more severe. According to Liu, et al, the advantage in film 2 is found attributed to both more surface defects as well as larger size of grains. In contrast, for film 3, it is opposite with film 2 with less surface defects, but smaller size of grain. Both film 2 and film 4 have surface defects, their good performance shows the existence of surface defect is very essential for a good cyclic stability.

2.6. Aniline polymer (PANI)
The combination with aniline polymer creates new path that are parallel to vanadium oxide chain, and largely adds convenience for the transport of electrons. There exists space charge effect between PANI chain, which serves as conductive phase, and vanadium oxide itself. The chains are held together by the increased interface area created by hydrogen bonding (NH—OV) between vanadium oxide and PANI, resulting in a greater effect on the electron conductivity\(^\text{[13]}\).  

![Figure 11](image-url)

**Figure 11.** In condition of 0.5M LiClO\(_4\), the Chronopotentiometric curves for [PANI]\(_{0.3}\) V\(_2\)O\(_5\) (line with circle) and V\(_2\)O\(_5\) (solid line)\(^\text{[14]}\)

As shown in Figure 11, V\(_2\)O\(_5\)/PANI shows better ability of lithium ion diffusion, and compared to the normal V\(_2\)O\(_5\) xerogel, it also has better conductivity of electrons. That is caused by the better charge capacity (313 Ah kg\(^{-1}\) for [PANI]\(_{0.3}\) V\(_2\)O\(_5\) and 234 Ah kg\(^{-1}\) for V\(_2\)O\(_5\))\(^\text{[14]}\). Huguenin et al. also find that in the condition of [PANI]0.3V\(_2\)O\(_5\), Lithium ions are the easiest to diffuse in the battery. More results show that when the molar ratio of PANI is 30%, the capacity ratio of V2O5/PANI nanofibers is stable at about 300 mAh g\(^{-1}\). The morphology of V\(_2\)O\(_5\)/PANI did not change significantly after 10 charges and discharges, but structural defects were found when only nanostructures were used.
3. Conclusion
In conclusion, it is found that the various derivatives for the original V$_2$O$_5$ compound are found to have promising implication possibilities. Most of the improvement focus on how to increase the diffusion of ions and electron in those cathode materials and the surface defects vacancies in order to increase the diffusion rate and to increase its capacity, while improvements are also made in order for increasing cyclability performance over charges and discharges. Samples such as V$_2$O$_5$ xerogel are easier to made while also have a better performance in terms of cyclability and discharge capacity. LVSB-10b combines vanadium oxide into glass compound and also shows promising future developments. Best ratio of these derived vanadium oxide compounds has also been discovered in terms of composition in cathode to maximize their performance. It is believed that V$_2$O$_5$ will achieve more developments in the near future and be able to play an important role in lithium battery cathode.

Disclosure statement
The author declares no conflict of interest.

References