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<td>Electrochemical lithium insertion behavior of combustion synthesized V2O5 cathodes for lithium-ion batteries</td>
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<td>Cheah, Yan Ling; Aravindan, Vanchiappan; Madhavi, Srinivasan</td>
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Lithium-ion batteries (LIB) are becoming one of the promising and attractive energy storage systems for electric vehicle (EV), hybrid and plug-in hybrid electric vehicle (HEV/PHEV) applications.1-5 Commercial LIB comprises LiCoO2 cathode and it is capable of delivering maximum capacity of $\sim 140$ mAh g$^{-1}$ corresponding to utilization of only 50% active material (Li$_{0.5}$CoO$_2$). Moreover, its poor thermal stability, high cost and material costs impede their potential use in large-scale applications. As a result, other cathode candidate chemistries such as olivine (LiFePO$_4$), spinel (LiMn$_2$O$_4$) and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ are also extensively investigated as possible alternative to LiCoO$_2$ for EV/HEV applications. For example, spinel LiMn$_2$O$_4$ suffers from severe Mn$^{4+}$ dissolution problem which attacks the counter electrode leading to degradation in electrochemical cell performance. Although LiFePO$_4$ is commercialized by few industries, it still suffers the poor conducting issues and also restricted by the lower operating potential. The layered LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ has high capacity, structural and thermal stability, and excellent cycling behavior. Yet, there exists, still, many issues to be addressed, such as low rate capability, considerable capacity loss during high current rates. In addition all the aforementioned cathode materials are capable of delivering discharge capacity less than 200 mAh g$^{-1}$. Hence, the search for high capacity cathodes is ongoing to power the high energy density LIB power packs for future EV/HEV applications.

Vanadium pentoxide (V$_2$O$_5$)$^{7-8}$ is an attractive cathode material for high energy density LIBs. Due to its layered structure, the insertion up to $\sim 3$ mol. Li$^{+}$ ion per formula unit (V$_2$O$_5$ $+$ Li$^{+}$ $+$ xe$^-$ $\leftrightarrow$ Li$_3$V$_2$O$_5$) leads to higher theoretical capacity of $\sim 400$ mAh g$^{-1}$. $^{7,8}$ V$_2$O$_5$ also has the advantages of low cost and abundant sources on the earth crust. However, problems such as severe capacity fading and poor rate capability prevent its use in commercial LIBs. Possibly, sluggish Li diffusion behavior, structural instability with lithium intercalation/de-intercalation and low electronic conductivity ($10^{-2}$ $-$ $10^{-3}$ S cm$^{-1}$) are main cause for such fading. Several approaches have been adopted to circumvent the aforementioned issues, such as modifying the crystal structure$^{6-11}$ to improve the Li$^{+}$ ion diffusion by creating more open structures$^{12,14,20}$ surface modification by conductive additives$^{15,17,18}$ and patterning the one dimensional nanostructures$^{12-14,16,19,26}$ As a result, research focus has been progressively moved away from bulk V$_2$O$_5$ particles. On the contrary, here an attempt has been made to synthesize sub-micron size V$_2$O$_5$ particles via assisted combustion technique by controlling various parameters to achieve high performance material. Further, we believe that, it is possible to achieve high specific capacity and also increase the cyclic stability of the V$_2$O$_5$ cathode using such sub-micron size particles by this route. The performance of V$_2$O$_5$ materials reported by other synthesis techniques are compared and given in Table I.

Urea combustion is a low temperature, relatively simple, cost effective and convenient method to obtain the materials with high yield. It involves exothermic reaction between urea (fuel) and nitrates (oxidizer) which drives the chemical synthesis.$^{73,74}$ Due to the self-propagating effect of this exothermic reaction, it enables the reaction to occur spontaneously at relatively lower temperatures leading to the formation of metal oxides thereby liberating nitrogen, hydrogen and oxygen gases.$^{25}$ It is well known that the electrochemical behavior of cathode materials strongly depends on the synthesis route, morphology and particle size (Table I). In this paper, the synthesis of V$_2$O$_5$ using urea assisted combustion is optimized and then a correlation between synthesis parameters including sintering temperatures, sintering time, ball milling with or without carbon on the electrochemical lithium intercalation have been studied and described in detail.

**Experimental**

V$_2$O$_5$ synthesis and characterization.—Vanadyl acetylacetonate (VO(acac)$_2$, 98%, Sigma-Aldrich, 2.65 g) was dissolved in nitric acid (69%, Honeywell, 5 mL) by heating at 60°C with continuous stirring resulting in a blue colored solution to which urea (Panreac, 1.8 g) was added until dissolution occurred. This mixture was heated at 300°C for 20 min to enable self-propagating combustion reaction. The obtained powder comprising the mixture of $\sim$5~wt% V$_2$O$_5$ and $\sim$46~wt% VO$_2$ in the crystalline phase (as confirmed by Rietveld refinement using Topas V3 software), as well as $\sim$20~wt% amorphous carbon. Hence, a subsequent heat-treatment is required to achieve highly crystalline and single phase V$_2$O$_5$ particles. The powder obtained from the combustion was sintered at various temperatures (300–600°C) for different durations ranging from 1–3 h in air to obtain single-phase V$_2$O$_5$. For comparison, V$_2$O$_5$ was also prepared by direct heating of 2.65 g of VO(acac)$_2$ at 600°C for 1 h without any combustion process. In addition, heat-treated (600°C sintered for 1 h) powder was ball-milled for further size reduction using high energy ball-mill (Spex, 8000D) for 1 h with and without carbon. For ball milling with carbon, active material to carbon ratio of 3:1 was maintained and no more carbon was included during the fabrication of the electrode. Morphological features of sintered V$_2$O$_5$ powders were studied using field emission scanning electron microscope (FE-SEM, JEOL).
Table I. Electrochemical performance of various V2O5 morphologies reported in literature.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Synthesis method</th>
<th>Initial discharge capacity (mAh g(^{-1})) at 0.1C</th>
<th>Capacity at nth cycle (mAh g(^{-1})) at 0.1C</th>
<th>Crystal size (nm)</th>
<th>Diameter (nm)</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofibers</td>
<td>Electrospinning</td>
<td>375</td>
<td>15.5</td>
<td>350</td>
<td>97</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>Nanofibers</td>
<td>Electrospinning</td>
<td>316</td>
<td>220 (20(^{th}))</td>
<td>70–80</td>
<td>500–1200</td>
<td>NA</td>
<td>20</td>
</tr>
<tr>
<td>Microspheres</td>
<td>Hydrolysis</td>
<td>437</td>
<td>245 (20(^{th}))</td>
<td>NA</td>
<td>NA</td>
<td>31.2</td>
<td>45</td>
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<tr>
<td>Nanorod</td>
<td>Thermal decomposition</td>
<td>266</td>
<td>240 (30(^{th}))</td>
<td>48</td>
<td>NA</td>
<td>NA</td>
<td>38</td>
</tr>
<tr>
<td>Nanowires</td>
<td>Electrospinning</td>
<td>390</td>
<td>201 (50(^{th}))</td>
<td>50</td>
<td>200–250</td>
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<td>14</td>
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<tr>
<td>Nanocomposite</td>
<td>Hydrothermal</td>
<td>239</td>
<td>209 (30(^{th}))</td>
<td>10–40</td>
<td>NA</td>
<td>NA</td>
<td>46</td>
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<tr>
<td>Thin film</td>
<td>E-beam irradiation</td>
<td>343</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>47</td>
</tr>
<tr>
<td>Nanowires</td>
<td>Hydrothermal</td>
<td>351</td>
<td>NA</td>
<td>NA</td>
<td>80–120</td>
<td>NA</td>
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<td>Nanorods</td>
<td>Annealing</td>
<td>260</td>
<td>260 (50(^{th}))</td>
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<td>13</td>
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<tr>
<td>Nanofibers</td>
<td>Electrospinning</td>
<td>360</td>
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<td>NA</td>
<td>40–70</td>
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<tr>
<td>Submicron belts</td>
<td>Sol-gel</td>
<td>346</td>
<td>240 (20(^{th}))</td>
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<td>Nanoscale single crystal</td>
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<td>300</td>
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<td>NA</td>
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<tr>
<td>Nanorods</td>
<td>Melt quenching</td>
<td>385</td>
<td>230 (50(^{th}))</td>
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<td>NA</td>
<td>NA</td>
<td>17</td>
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<tr>
<td>Microspheres</td>
<td>Solution method</td>
<td>319</td>
<td>160 (45(^{th}))</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>47</td>
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<tr>
<td>Nanowires</td>
<td>Hydrothermal</td>
<td>327</td>
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<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>50</td>
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<tr>
<td>Nanopowder</td>
<td>Urea combustion</td>
<td>320</td>
<td>230 (50(^{th}))</td>
<td>200</td>
<td>NA</td>
<td>3 Current work</td>
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Electrode fabrication process.— The composite cathodes were prepared by mixing active material (V2O5), binder (Kynar 2801), and conductive additive (Super P Li carbon, Timcal) in the weight ratio 60:20:20, respectively, using 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich) solvent for binder to form slurry. The resulting viscous slurry was stirred continuously and subsequently coated on aluminum foil (Hohsen Corporation) using a doctor blade. The slurry-coated Al foils were dried in a vacuum oven for several hours to remove the solvent molecules and pressed in between the twin roller to provide good adherence toward current collector. Then the dried composite V2O5 electrodes were punched out with 16 mm diameter blanks and same area of lithium foil (∼ 0.59 mm thick, Hohsen Corporation, Japan) was used as the counter electrode. The lithium intercalation properties were studied in half-cell configuration using CR 2016 coin cells assembled in an Argon-filled glove box (MBraun). The 1 M LiPF6 in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 wt%, Danvac) as electrolyte and separated by Celgard 2400.

Galvanostatic discharge-charge cycling was carried out at room temperature using battery tester systems (Neware). Cyclic voltammetry (CV) studies were conducted in the same two electrode configuration at the scan rate of 0.1 mV s\(^{-1}\), in which metallic lithium act as counter and reference electrode. Both CV and electrochemical impedance spectroscopic (EIS) studies were conducted using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiotstat. EIS studies were carried out on equilibrated cells before cycling, by applying a.c. amplitude of 10 mV over the frequency range 100 kHz to 5 mHz at open circuit potential, at room temperature. The Nyquist plots Z' vs. Z" were derived and analyzed using Zplot and Zview software (Version 2.2, Scribner Associates Inc., USA).

Results and Discussion

Morphological and compositional studies.— FE-SEM recorded on V2O5 powder sintered at 600 °C for 1 h in air (Figure 1a) revealed irregular shape V2O5 particle morphology with size ranging from 200–800 nm. The TEM image in Figure 1b shows the formation of well crystalline V2O5 particle and it was confirmed by SAED patterns. The observed diffraction spots of the crystal can be indexed to the (410) and (110) planes of the planes of the Shcherbinaite V2O5 phase.

A representative X-ray powder diffraction (XRD) pattern evaluated by Rietveld refinement is presented in Figure 2a. The family of XRD patterns of sintered V2O5 powders are collected and presented in Figure 2b. Herein, the following labeling system has been used to describe the synthesized V2O5 powders, for example, VUC 600-1 here. VUC represents V2O5 by urea combustion, sintered at 600 °C for duration of 1 h. Rietveld refinements are carried out for all the powders prepared using TOPAS software. Observed reflections indicate the formation of single phase orthorhombic V2O5 corresponding to the layered Shcherbinaite structure (Pnm\(_2\)\(_1\)), without any impurity phases. Calculated lattice parameters and crystallite sizes obtained from Scherrer equation are presented in Figure 3a–3c and 3d, respectively. It is worth to mention that, increasing sintering temperature results increase of lattice parameter values. Such increasing trends are also observed while increasing sintering time as well. Nevertheless, the observed values for lattice parameters a and c are slightly less than the literature values (JCPDS 89-2482 a = 11.544(2) Å, b = 4.383 (1) Å and c = 3.571 (1) Å) given in the corresponding Figures 3a–3c, whereas the lattice parameter b value is slightly higher than reported. Furthermore, increasing the sintering temperature from 300–600 °C leads to a nearly exponential increase in crystallite size and it is clearly seen from Figure 3d. Overall increase in sintering duration (for example, 2 or 3 h) reveals noticeable increase in lattice parameter values and this effect is also more pronounced at higher sintering temperatures (400, 500 and 600 °C). Also, higher sintering temperature leads to increase in crystallite size, as given in Figure 3d. As the crystallite sizes obtained from the refinement data are much smaller than that observed from FE-SEM analysis and it is possible reason that the agglomeration of the crystallites may have occurred. The crystallite sizes are compared with V2O5 particles obtained at

JSM-7600F) with an accelerating voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100F) in high resolution mode operating at 200 kV. Structural properties of V2O5 powders were examined using Bruker X-ray diffractometer using Cu-K\(_α\) radiation between 10 to 80°. The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld refinement\(^{28,29}\) within the software Topas V3 (Bruker-AXS), using fundamental parameters approach.\(^{30}\) Thermo-gravimetric analysis (TGA) of the as-combustion synthesized powder was recorded using Perkin Elmer Q500 with the scan rate of 10°C min\(^{-1}\) from room temperature to 850°C. Fourier transform infrared spectroscopy (FT-IR) was recorded on KBr pellets of sintered V2O5 powder using a Perkin Elmer Spectrum GX FT-IR in the range of 4000 to 400 cm\(^{-1}\). Brunauer-Emmet-Teller (BET) surface area studies were also conducted using Nova 3200e surface area and porosity analyser.

...
600°C for 1 h and subsequently ball-milled for 1 h. Crystallite sizes of the ball-milled particles are reduced from 200 to 20 nm. At the same time, when the particles are ball-milled with conducting carbon (3:1 w/w), the average crystallite sizes are further reduced from 200 to 28 nm.

It is known that the detection of residual organic molecules in V₂O₅ particles by XRD analysis is complicated. Hence, thermogravimetric studies are carried out and presented in Figure 4a. Noticeable amount of (∼20 wt%) weight loss is observed from the TGA of the as-combustion synthesized powder around 400°C. This weight loss is an indication of the complete phase transformation from VO₂ to V₂O₅ occurs during sintering >400°C in air. In order to confirm the formation of organic-moieties-free V₂O₅ powders, FT-IR spectra has been recorded for all the powders and selectively presented in Figure 4b. All the recorded FT-IR spectra of V₂O₅ comprise three characteristic bands at 1009, 817 and 527 cm⁻¹, irrespective of the sintering temperature. The sharp peak around 1009 cm⁻¹ corresponds to the V=O stretching vibration and broad peaks at 827 and 527 cm⁻¹ are assigned to asymmetric and symmetric stretching modes of V-O-V bonds respectively. Few additional peaks are observed in the case of 300°C sintered materials for all durations. The peaks around 1392, 1612 and 1717 cm⁻¹ are related to the presence of urea, as well as O-H bond vibrations. This clearly indicates that the urea is not fully decomposed during the sintering process at 300°C, whereas
investigated and presented. The V2O5 obtained from the sintering due to the occupancy of Li insertion of lithium ions into V2O5 layers results the phase transformation of V2O5 to Li/V2O5 leading to distortion in layered structure whereas those prepared at 300 °C showed highest surface area of 6–11 m² g⁻¹. As expected, the ballmilling procedure with carbon yielded slightly higher surface area for V2O5 particles of 19 m² g⁻¹.

Electrochemical studies.— Electrochemical properties of the synthesized V2O5 particles are evaluated by means of galvanostatic and potentiostatic modes in half-cell (Li/V2O5) configuration. All the half-cells are cycled between 1.75–4.0 V at 0.1 C in room temperature conditions by galvanostatically. As described in our previous work, the insertion of lithium ions into V2O5 layers results the phase transformation of V2O5 to LiV2O5 leading to distortion in layered structure due to the occupancy of Li⁺ ions into the spaces between the layers of VO₆ octahedral unit. The galvanostatic cycling studies are carried out for all the temperature conditions and sintering durations at 0.1 C rate and we are presenting the best performing materials in each sintering temperature. The V2O5 powders obtained from sintering at 600 °C for 1 h showed best cycling performance, whereas material sintered at 300 C for 2 h (VUC 300-2) presented a poor performance among the materials prepared in this work. The detailed analysis will be discussed in later sections.

Cyclic voltammograms (CV) of Li/V2O5 cells (VUC 600-1 and VUC 300-2) are collected in the range of 1.75–4.0 V vs. Li/Li⁺ at the slow scan rate of 0.1 mV s⁻¹ to understand the phase transformation occurring during lithium intercalation/de-intercalation into VO₂ layers and presented in Figure 5. The following equation indicates the typical intercalation mechanism in V₂O₅ matrix,

\[ V_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xV_2O_5 \]  

The Li/V₂O₅ cells are first discharged to intercalate the Li⁺ ions in to V₂O₅ lattice. In the 1st cycle (Fig. 5a), several oxidation/reduction peaks are observed for both VUC 600-1 and VUC 300-2 powders and corresponding to the intercalation/de-intercalation processes of Li⁺ in V₂O₅. The reduction (cathodic) peaks are observed at ~3.37, ~3.16, ~2.22, and ~1.81 V vs. Li/Li⁺, whereas two oxidation peaks only observed at ~2.70 and ~3.45 V vs. Li/Li⁺, respectively in both materials with different current densities. This variation in the current density may attribute to the nature of crystallinity of materials synthesized. The appearance of cathodic peaks indicates that the reduction of V⁵⁺ in V₂O₅ takes place as a multistep process within the voltage range 1.75 to 4.0 V.²⁰ The cathodic peaks at ~3.37 and ~3.16 V indicates the reduction of V⁵⁺ to V⁴⁺, and this reduction reveal the formation of Li,V₂O₅ phase

There is no such peaks are observed in the samples heat treated at 400, 500 and 600 °C for all durations indicating the complete degradation of organic molecules. Hence, it can be concluded that high purity V₂O₅ particles could be obtained the sintering temperature above 300 °C. The observed FT-IR spectrum is in good agreement with TGA observations. BET surface area analysis of the synthesized V₂O₅ powders are investigated and presented. The V₂O₅ obtained from the sintering temperatures of 600 and 500 °C for 1–3 h exhibiting lowest surface area (~3 m² g⁻¹) of the materials prepared. However, sintering the materials at 400 °C gives rise to higher surface area of 6–8 m² g⁻¹ whereas those prepared at 300 °C showed highest surface area of 6–11 m² g⁻¹. The apparent FT-IR spectrum is in good agreement with TGA observations.

The Li/V₂O₅ cells are cycled between 1.75–4.0 V at 0.1 C in room temperature conditions by galvanostatically. As described in our previous work, the insertion of lithium ions into V₂O₅ layers results the phase transformation of V₂O₅ to LiV₂O₅ leading to distortion in layered structure due to the occupancy of Li⁺ ions into the spaces between the layers of VO₆ octahedral unit. The galvanostatic cycling studies are carried out for all the temperature conditions and sintering durations at 0.1 C rate and we are presenting the best performing materials in each sintering temperature.

Figure 4. Fourier-transform infrared spectra (FT-IR) of samples sintered at 300, 400, 500 and 600 °C for 3 h respectively.

Figure 5. Cyclic voltammograms of VUC 300-2 and VUC 600-1 showing (a) first cycle, (b) second cycle and (c) 20th cycle, in which metallic lithium configuration with the scan rate of 0.1 mV s⁻¹ between 1.75–4.0 V vs. Li/Li⁺.
V$_2$O$_5$ formula unit. However, reversible reactions are takes place only in the potentials at $\sim$2.70 and $\sim$3.45 V vs. Li/Li$^+$ during anodic scan.

During subsequent cycles (Figure 5b & 5c), only one main well-defined oxidation/reduction pair is present for VUC 600-1. Further, the reduction peak is shifted to $\sim$2.42 V, whereas oxidation peak remains at $\sim$2.84 V vs. Li/Li$^+$. These peaks are intact upon further cycling to 20 cycles, indicating the reversibility of the redox reactions. Whereas, the CV of VUC 300-2 is concerned, in the first cycle, it also undergoes similar reduction (cathodic) process of VUC 600-1 and exhibiting characteristic potentials at $\sim$3.4, $\sim$3.18, $\sim$2.2 and $\sim$1.9 V vs. Li/Li$^+$ respectively. In addition to above, two more additional reduction peaks can be observed at $\sim$2.46 and $\sim$2.81 V. These extra peaks can be attributed to the unwanted side reactions of organic impurities present in the VUC 300-2 sample. However, it shows the prominent oxidation peak at $\sim$2.68 V in the first cycle rather than VUC 600-1. In the subsequent cycles (Figure 5b & 5c), two reduction peaks remains at $\sim$2.49 and $\sim$2.81 V vs. Li/Li$^+$. The difference in the oxidation peaks of VUC 300-2 ($\sim$2.68 V) and VUC 600-1 ($\sim$2.84 V) in subsequent cycles may also be attributed to the incomplete formation of crystalline V$_2$O$_5$ phase, which provides sluggish kinetics during insertion/extraction of Li$^+$ ions and presence of impurities cannot be excluded (Figure 6b). In turn, incomplete reduction of V$_5^+$ to V$^{4+}$ and V$^{3+}$ takes place which leads to considerably less initial discharge capacity (250 mAh g$^{-1}$) when compared to VUC 600-1 at 0.1 C (320 mAh g$^{-1}$). In subsequent cycles, plateaus are not prominent in both cases and exhibiting the monotonous charge and discharge curves, which indicates that the Li$^+$ intercalation/de-intercalation occurred reversibly in mixed phases of Li$_x$V$_2$O$_5$ formed after the first discharge. The specific discharge capacities of 320 and 250 mAh g$^{-1}$ are obtained for first and second cycles, respectively for VUC 600-1. The VUC 300-2 delivered the discharge capacities of 250 and 240 mAh g$^{-1}$ for first and second cycle. This improved capacity retention of VUC 300-2 rather VUC 600-1 is ascribed to the incomplete crystallization of V$_2$O$_5$, thereby preventing the faster diffusion of Li$^+$ ions and presence of impurities cannot be excluded (Figure 6b). The first discharge plateau at 3.18 V vs. Li/Li$^+$ vs. Li/Li$^+$ is believed to be the transformation of δ-Li$_x$V$_2$O$_5$ to ε-Li$_x$V$_2$O$_5$ phase. Further discharging into 1.75 V causes the irreversible formation of ε-Li$_x$V$_2$O$_5$ and this holds good agreement with reduction potential in the CV $\sim$1.81 V vs. Li/Li$^+$. In the case of VUC 300-2, the first discharge profile plateaus are not prominent when compared to VUC 600-1, which can be attributed to the incomplete crystallization of V$_2$O$_5$, thereby preventing the faster diffusion of Li$^+$ ions and presence of impurities cannot be excluded (Figure 6b).

The galvanostatic cycling profiles of VUC 600-1 and VUC 300-2 coin cells cycled between 1.75–4.0 V vs. Li/Li$^+$ at 0.1 C rate (35 mA g$^{-1}$) at room temperature are shown in Figure 6. Both samples show multiple plateaus during first discharge, which is consistent with the CV analysis and data reported elsewhere. Such plateaus are more prominent in the VUC 600-1 cell when compared to VUC 300-2 (Figure 6a). The first discharge plateau occurs at 3.18 V vs. Li/Li$^+$; this can be correlated to the reduction of V$_5^+$ to V$^{4+}$ to enable the intercalation of Li into the layered V$_2$O$_5$. As a result, a mixture of α-δ-Li$_x$V$_2$O$_5$ phases are formed (eqn. 2). Upon further discharge, two stable plateaus at $\sim$2.24 and $\sim$1.90 V are observed. The plateau at $\sim$2.24 V is an indication of the formation of δ-Li$_x$V$_2$O$_5$ and further V$^{4+}$ is partially reduced to V$^{3+}$ forming the δ- and ε-Li$_x$V$_2$O$_5$ mixed phase. The plateau $\sim$1.9 V is believed to be the transformation of δ- Li$_x$V$_2$O$_5$ to ε-Li$_x$V$_2$O$_5$ phase. Further discharging into 1.75 V causes the irreversible formation of ε-Li$_x$V$_2$O$_5$ and this holds good agreement with reduction potential in the CV $\sim$1.81 V vs. Li/Li$^+$. As mentioned earlier, all V$_2$O$_5$ powders obtained using urea combustion synthesis were cycled galvanostatically at 0.1 C rate (35 mA g$^{-1}$) and presented in Figure 7. Other than VUC 600-1 and VUC 300-2, the cycling performance of other samples VUC 400-3 (sintered at 400°C for 3 h) and VUC 500-1 (sintered at 500°C for 1 h)
are also presented in Figure 7a. The powder VUC 600-1 delivered initial specific discharge capacity of 320 mAh g\(^{-1}\) and maintains stable discharge capacity of \(\sim 230\) mAh g\(^{-1}\) (72% of initial discharge capacity) after 50 cycles. Such initial specific capacity is comparable to those reported in literature\(^b\),\(^c\),\(^d\),\(^e\),\(^f\) especially for one-dimensional nanostructures, as given in Table I. Despite the relatively lower BET surface area, VUC 600-1 has comparable initial discharge capacity to 1D nanostructures, and along with much improved cyclic retention properties.

On the other hand, VUC 500-1 presented an initial specific discharge capacity of 270 mAh g\(^{-1}\) and 59% of its initial discharge capacity only retained after 50 cycles. Similarly, VUC 400-3, 300-2 exhibited initial specific discharge capacity of 350 and 250 mAh g\(^{-1}\) respectively. The capacity retention of VUC 400-3 and 300-2 is found to be 49 and 50% respectively after 50 cycles.

In order to study the effect of particle size on the electrochemical properties \(V_2O_5\) powders, the VUC 600-1 is subsequently ball-milled using high energy milling with or without carbon. The cycling performance of the ball-milled and native \(V_2O_5\) are illustrated in Figure 7b. The ball-milled powder showed slightly lower initial discharge capacity of 260 mAh g\(^{-1}\) than the native compound, but an improved cyclic retention of 77% after 50 cycles is noted. Similarly, the powder, which is ball-milled with conductive carbon showed initial capacity of 245 mAh g\(^{-1}\) and better capacity retention of 82% is observed after 50 cycles than rest of its counterparts and this result is expected. Apart from the size reduction, ballmilling with carbon particles provides enhanced contact toward active material particulates than conventional mixing and thereby improving the performance of the cell. The powder morphology of the sample enables further improvement of cycling stability by a simple ballmilling procedure, which is not possible for other nanostructures as mentioned in Table I, as the morphology would be destroyed.

Furthermore, the role of combustion synthesis on the performance of \(V_2O_5\) is compared by direct sintering of the starting material at 600°C for 1 h (Non-Urea Combustion, NUC 600-1). The electrochemical properties of above material was evaluated and compared with VUC 600-1 and commercially available material. The NUC 600-1 cell delivered the lower initial discharge capacity of 220 mAh g\(^{-1}\) when compared to 320 and 278 mAh g\(^{-1}\) for VUC 600-1 and commercial powders respectively. The capacity retention of VUC 600-1 and NUC 600-1 powders are almost same \(\sim 71%\) after 50 cycles. However, the urea combustion synthesis leads to slightly increased initial discharge capacity than rest.

Based on the electrochemical performance of \(V_2O_5\) particles prepared by various conditions as stated above, the VUC 600-1 powder rendered better electrochemical performance among the samples tested. The same material has been subjected to rate performance studies with different C-rates conducted between 1.75 to 4.0 V and presented in Figure 8 with two duplicate cells. In both cells, it is evident that specific discharge capacity tends to decreases slowly at low current rate (0.1 C) during prolonged cycling. However, capacity fading is significantly improved when the cells are cycled at high currents, for example 0.5 or 1 or 2 C-rates. For the rate performance studies, the test cells are initially cycled to 50 cycles at 0.1 C and subsequently employed for high current rates. In the first cell, the C rate is increased from 0.1 to 1 C, the specific discharge capacity is decreased from 190 to 125 mAh g\(^{-1}\) and the capacity is maintained over 99% for 10 cycles. Such behavior is expected in high current rates, while cycling the cell at high C rates, the surface of active material only involves the reaction rather than bulk. When the C rate is switched back to 0.1 C, the capacity is retained from 120 to 190 mAh g\(^{-1}\).

Similarly, in the duplicate cell, the C-rate is increased from 0.1 to 0.2 C, a small amount of capacity fading (from 175 to 165 mAh g\(^{-1}\)) is noted. With further increase in current to 0.5, 1 and 2 C rates, the cell delivered excellent discharge capacitive properties with negligible capacity fade. Finally, the current rate is relaxed to 0.1 C, and the discharge capacity is retained for its original state and maintained at 145 mAh g\(^{-1}\) for after 20 cycles. From the above analysis, it can be concluded that the \(V_2O_5\) prepared at 600°C for 1 h by urea combustion
The experimental data are subjected to a non-linear least square fitting procedure and equivalent circuit parameters are obtained for experimental spectra and lines indicate fitted data of above model.

The Nyquist plots of fresh cells (a) VUC 600-1, 500-1, 400-3 and 300-2, (b) VUC 600-1, ball-milled VUC 600-1, ball-milled VUC 600-1 with carbon and NUC 600-1 and (c) equivalent circuit model used. Symbols represent experimental spectra and lines indicate fitted data of above model.

The Rb is also increased to 323 μF when compared to the combustion sample VUC 600-1. The RSEI ct and CPESEI values are noted when compared to native compound. The Rb and CPEb are also reduced to 46 Ω and 5 mF respectively, compared to VUC 600-1. This may be correlated to the decrease in the porosity of the ball-milled sample. Similarly, Warburg resistance is also noticeably reduced from ∼1.75 kΩ to 25 mΩ. The decrease in Warburg impedance values indicate that diffusion pathways have been increased in the ball-milled sample due to the reduction in the particles size. Further ballmilling with conductive carbon (Super P Li) to the VUC 600-1 sample leads to the increase in RSEI ct and CPESEI values to ∼1.30 kΩ and 17 μF respectively from ball milled powders. This is believed to be due to the capacitive effect of Super P Li carbon, in which ballmilling further enabled more homogeneous mixing of the active material and conductive species. The Rb is also increased to 323 Ω, however, there is no major variation in the CPEb value (∼5 mF) upon addition of Super P Li carbon. The decrease in Warburg resistance to 1.7 mΩ indicates that the addition of conductive carbon leads to a faster diffusion of lithium ion during electrochemical reaction, which has been reflected in the cycling performance of the cells.

In addition to the above, the powder NUC 600-1 showed highest RSEI ct values (545 Ω) and capacitive effect of the interphase is reduced from 32 μF to 23 μF when compared to the combustion sample VUC 600-1. The bulk resistance is also increased to 194 Ω whereas bulk capacitance (CPEb) is reduced to 2 mF. Finally, the high Warburg resistance (Wb) ∼13.9 kΩ indicated the large decrease in number of diffusion pathways, which results in poor performance during cycling.

From the EIS analysis, it can be concluded that larger particle size of VUC 600-1 enabled better cycling stability, though it exhibited slightly lower initial discharge capacity when compared to rest of the samples prepared at different conditions. Ball-milling is one of the approaches to reduce the particle size, which increases the contribution toward more robust surface film formation via larger available area. However, overall bulk resistivity is reduced when compared to VUC 600-1. Hence, ballmilling of V2O5 powder increases number of diffusion pathways for Li+ ion transport, which is observed from the improved capacity retention properties. Moreover, urea combustion method provides improved the capacitive properties of V2O5 powders and also increased the electro-active surface which is reflected in the reduced Warburg resistance value when compared to that of non-combustion synthesized sample NUC 600-1. This result is also in good agreement with higher initial capacity and cycling profile observed for VUC 600-1 when compared to NUC 600-1.

Conclusions

Sub-micron size V2O5 particles are obtained via one-step urea combustion synthesis method and the parameters like sintering tem-
perature and duration has been optimized. FE-SEM showed the formation of particles in the range of 200–800 nm. The XRD pattern reveal the formation of single phase V$_2$O$_5$ particulates and FT-IR studies also enable improved capacity and rate capabilities of V$_2$O$_5$. Electrochemical impedance studies bring about new insights to the kinetics of urea-combusted V$_2$O$_5$ and provided explanation for the cyclic retention properties of V$_2$O$_5$ during the Li intercalation/de-intercalation processes.

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