High-Performance Polyoxometalate-Based Cathode Materials for Rechargeable Lithium-Ion Batteries

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Rechargeable lithium batteries show great promise for high-density energy storage for applications ranging from consumer electronics to electric vehicles and grid balancing.[1] Cathode materials in these batteries are typically oxides of transition metals, which undergo oxidation to higher valences when lithium is removed.[2] Current cathode materials for rechargeable Li-ion batteries are still mainly based on bulk transition metal oxides:[3] distorted rock-salt α-FeOFe₂ structures,[4] spinel structures,[5] and olivine structures.[6] However, either the low Li-ion mobility and/or the low electronic conductivity of these compounds hamper a high power density output, unless particle sizes are reduced to the nano-scale.[7] or carbon coating/doping strategies are employed.[8] In order to satisfy the increasing demand for high power density and energy density, new cathode materials capable of multielectron redox reactions and that enable more rapid Li-ion transportation (while still displaying stable cycling performance) are required.[9]

Recently, polyoxometalates[10] and metal–organic frameworks (MOFs)[11] have been shown to have potential as the cathode materials for rechargeable batteries. For example, [Fe₃[OH]₀₈F₀₂₂[O₂CC₆H₄CO₂]·H₂O (MIL-53(Fe)-H₂O) has been used as the cathode material for Li-based batteries, although the capacity was limited by the low number of electrons (not more than one electron per formula unit) involved in the reversible redox reaction.[12] Polyoxometalates are promising multifunctional materials which have numerous applications in catalysis, photoluminescence, as single molecule magnets, and as proton-conductive materials.[13] One of the most important features of POMs is the ability to configure or tailor their redox properties, which allows the development of new functional systems, such as metal–oxide–semiconductor (MOS) flash memory devices[14] and mediators for electrochemical water splitting.[15]

Polyoxometalates have already demonstrated some promise as the cathode in lithium batteries,[10] for example where the active cathode material was phosphomolybdate ([PMo₁₂O₄₀]³⁻) and the anode was lithium metal.[10] In operando Mo K-edge XAFS measurements on these cathodes revealed that [PMo₁₂O₄₀]³⁻ functioned as an “electron sponge,” cycling reversibly by 24 electrons between [PMo₁₂O₄₀]³⁻ and [PMo₁₂O₄₀]²⁻ during charging/discharging.[16] However, the energy density and power density metrics of these cathode materials were limited by the slow rate of charge/discharge: capacities in excess of 200 mA h g⁻¹ could be obtained after ten cycles, but only at a low current of 1 mA.

In view of this prior work, we hypothesized that vanadium-based polyoxometalates would make excellent cathode materials candidates, exhibiting high capacities and rapid charging/discharging while also providing a larger operating voltage than the polyoxometalates previously explored for this purpose. Herein, we show that the polyoxovanadate Li₇[V₁₅O₃₆(CO₃)] has multielectron redox properties suitable for producing cathode materials with a specific capacity of 250 mA h g⁻¹, and energy and power densities of 1.5 kW h L⁻¹ and 55 kW L⁻¹ respectively in Li-based batteries.

Li₇[V₁₅O₃₆(CO₃)] was prepared according to an adapted literature procedure[17] and its crystal structure is shown in Figure 1a. The spherical anion {V₁₅O₃₆} of Li₇[V₁₅O₃₆(CO₃)] has a “hollow sphere” structure with an encapsulated CO₃²⁻ group, which has the high crystallographic symmetry D₃h, formed by linkage of 15 tetragonal VO₅ pyramids. The 15 V atoms are arranged on the surface of a sphere at a distance of 343 ± 10 pm from the center of the cluster. {V₁₅O₃₆} formally contains eight V⁴⁺ centers and seven V⁵⁺ centers. Six VO₅ pyramids are each linked via three edges and two corners, six further are each linked via two edges and three corners, and three are each linked via two edges and four corners. All µ₁-O atoms concomitantly participate in two edge linkages and one corner-linkage; the µ₂-O atoms form a corner linkage. Such linkages lead to the formation of cubic cages with a cluster anion at each corner, which is further arranged along the three channels occupied by water and cations (see Figure S1 in the Supporting Information). These polyoxovanadate clusters also show good thermal stability when dried at 200 °C under vacuum overnight (Figure S2, Supporting Information). As shown in the TEM image of Figure 1b, the dehydrated polyoxovanadate clusters form ultrafine particles less than 5 nm in diameter, probably
therefore consisting of some tens of individual polyoxovanadate clusters. Mass spectroscopy of the \(\text{V}_{15}\text{O}_{36}\) clusters before and after this high-temperature treatment confirms that the structure of the \(\text{V}_{15}\text{O}_{36}\) clusters is retained after heating (i.e., they do not coalesce to form bulk oxide), which is also consistent with the results of FTIR (see Figure S3 and S4 in the Supporting Information).

Interestingly, \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ shows reversible redox behavior over the large voltage window 4.0–1.9 V versus Li/\(\text{Li}^{+}\), when used in a half-cell with a metallic Li anode with 1 M \(\text{LiPF}_{6}\) in ethylene carbonate (EC) + dimethyl carbonate (DMC) + ethyl methyl carbonate (EMC) (1:1:1, v/v) as the electrolyte. As illustrated by the cyclic voltammetry (Figure 2a), the polarization \(\Delta E\) between the reduction and oxidation processes is small and the CVs of the first and second sweeps overlay well, indicating functional stability for the cathode and suggesting that \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ does not decompose during cycling. Meanwhile, the redox peaks are distributed in two voltage zones: 2.2–2.6 V and 3.3–3.7 V. In order to understand the cycling behavior of \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\, galvanostatic charging–discharging was carried out to calculate the number of \(\text{Li}^{+}\) ions translocating during these redox processes. As shown in the galvanostatic charging–discharging profiles in Figure 2b, \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ delivers an initial discharging capacity of 140 mA h g\(^{-1}\) at a current density of 50 mA g\(^{-1}\). When charging back to 4.0 V versus \(\text{Li}^{+}/\text{Li}\), a reversible charging–discharging capacity of 250 mA h g\(^{-1}\) is obtained for these \(\text{V}_{15}\text{O}_{36}\) clusters. According to the equation:

\[
Q = \frac{nF}{3.6M_w} = \left(\frac{96500n}{3.6M_w}\right)
\]

where \(Q\) is the reversible charging–discharging capacity, \(n\) is the number of electrons passed during the redox reaction, and \(M_w\) is the molecular weight of \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ (\(M_w = 1448.7\) g mol\(^{-1}\)), the translocation of each \(\text{Li}^{+}\) to/from the polyoxovanadate cluster contributes a capacity of around 18.5 mA h g\(^{-1}\). As a result, we calculate that between seven and eight \(\text{V}^{V}\) centers (140/18.5) are electrochemically reduced to \(\text{V}^{IV}\) during the first discharging process, and that 13.5 \(\text{V}^{V}\) centers (250/18.5) undergo electrochemical oxidization during the subsequent charging process (and in the charge–discharge processes thereafter). The theoretical specific capacity for \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ within this voltage window can then be calculated by taking \(n\) to be 14 (the next nearest integer number of electrons), and feeding this number back into the equation above to find a theoretical specific capacity for \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ of 259 mA h g\(^{-1}\).

\(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ shows high rates performance when tested as a cathode over the voltage range 1.9–4.0 V (Figure 3a). The polarization of the discharging plateaus is not great when subjected to a high charging–discharging current density, and 170 mA h g\(^{-1}\) can be obtained at a high discharge rate of 2 A g\(^{-1}\), and a specific capacity of around 140 mA h g\(^{-1}\) is possible at the even more extreme current density of 10 A g\(^{-1}\). This excellent rates and cycling performance at high current density (with almost 100% Coulombic efficiency over 100 cycles, Figure 3c) could be due to the ultrafine size of the \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ active material (Figure 1b), and ensure a high power density output of 25.7 kW kg\(^{-1}\) with an energy density output of 370 W h kg\(^{-1}\) (Figure 3b). In terms of volumetric densities (and taking the crystal density of \(\text{Li}_{7}\[\text{V}_{15}\text{O}_{36}\text{(CO}_{3}\text{)}\]\ to be 2.15 g cm\(^{-3}\)),

![Figure 1.](image1)

![Figure 2.](image2)

![Figure 3.](image3)
Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] exhibits energy and power densities of 1.5 kW h L$^{-1}$ and 55 kW L$^{-1}$.

The kinetics of the various reversible redox processes of Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] were studied by the potentiostatic intermittent titration techniques (PITT) method.$^{[12,18]}$ As shown in Figure 4, the chronoamperometric response of Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] indicated no obvious bell-shape variation, suggesting that Li-ion migration is not kinetically limited by a two-phase interface in these electrodes. In fact, all the current curves decay gradually during each potential step and almost follow a Cottrell-type law, indicative of a solid solution insertion process kinetically limited by Li$^+$ diffusion. This behavior is significantly different from the intercalation processes found in the bulk oxides commonly used in Li-ion batteries, such as the LiMPO$_4$.$^{[19]}$ Li$_x$V$_2$O$_5$ generally displays four or five plateau regions, each one corresponding to a two-phase process, while Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] has similar redox behavior but corresponding to a solid solution insertion process. As a result, a methodology based on galvanostatic intermittent titration techniques (GITT) and electrochemical impedance spectroscopy (EIS) $^{[21]}$ can be used to estimate the apparent chemical diffusion coefficient of Li$^+$ in the Li$_7$[V$_{15}$O$_{36}$(CO$_3$)]-based cathode. As shown in Figure S6 (Supporting Information), the $D_{Li^{+}}$ values are comparatively high over the voltage range 2.2–3.9 V, with values ranging from $1.4 \times 10^{-10}$ to $2.3 \times 10^{-7}$ cm$^2$ s$^{-1}$, showing that the mobility of Li$^+$ ions remains high in this material when compared to other bulk metal oxides such as LiCoO$_2$ ($10^{-12}$ to $10^{-10}$ cm$^2$ s$^{-1}$ over the voltage range 3.85–4.35 V$^{[22]}$ and V$_2$O$_5$ ($10^{-11}$ to $10^{-8}$ cm$^2$ s$^{-1}$ over the voltage range 3.2–3.45 V$^{[23]}$). The progressively decreasing concentration of vacant sites available for Li$^+$ as intercalation of Li$^+$ proceeds would cause a lower diffusion coefficient in LiCoO$_2$, while the variation of diffusion coefficient with voltage in Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] suggests a decreasing number of uptake/removal sites for Li$^+$ on the surface of the cluster. Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] is an open-framework material consisting of multiple individual polyoxovanadate clusters, each of which has multiple vanadium centers undergoing redox cycling, and as such it may have a rather different Li-ion transportation mechanism to that displayed in traditional bulk metal oxide cathodes. The rapid diffusion of Li$^+$ in the Li$_7$[V$_{15}$O$_{36}$(CO$_3$)]-based cathodes suggests that the uptake/removal processes of Li ions in polyoxometalate-based batteries are somewhat easier than the intercalation/deintercalation processes at work in bulk metal oxides. Moreover, the electronic conductivity of the Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] cathode material was found to be $1.12 \times 10^{-6}$ S cm$^{-1}$ at 20 °C (Figure S7, Supporting Information), which also compares favorably with the currently available cathode materials (around $1 \times 10^{-7}$ S cm$^{-1}$ for LiFePO$_4$ and around $1 \times 10^{-8}$ S cm$^{-1}$ for LiCoO$_2$).

Control experiments using equivalent loadings of LiVO$_3$ and V$_2$O$_5$ (two likely decomposition products of Li$_7$[V$_{15}$O$_{36}$(CO$_3$)]) showed that these simpler oxides of vanadium exhibit impaired and/or less stable behavior than Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] when used as the base materials for Li battery cathodes (see Figure S8 and S9 in the Supporting Information). Considering the reversibility of the charge–discharge processes of the Li$_7$[V$_{15}$O$_{36}$(CO$_3$)]-based electrodes, it thus seems likely that higher nuclearity polyoxometalate clusters are required in order to achieve the activity observed in the batteries studied herein. These control experiments also suggest that decomposition of the polyoxometalate clusters to these simpler oxides does not occur to a significant degree over the number of cycles studied. In a similar way, cathodes containing Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] that had been cycled in a battery ten times were extracted with water, and mass spectrometry was performed on the material dissolved out of these electrodes. These data (see Figure S10 in the Supporting Information) show that the molecular polyoxometalate cluster is still present in the cathode after multiple cycling events.

In conclusion, our studies of Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] have identified polyoxovanadates as a new class of potential cathode material for future high energy and power density Li-ion rechargeable batteries. Rapid lithium-ion diffusion and good electron conductivity in Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] should allow rapid charging and discharging of the resulting battery, and we have shown that a power density output of 25.7 kW kg$^{-1}$ ($55$ kW L$^{-1}$) is possible with this material. In contrast to the bulk oxides traditionally used as cathode and anode materials in rechargeable batteries, the polyoxometalate investigated herein can undergo multielectron reduction while still retaining its cluster structure. On account of the wealth of readily accessed polyoxometalate structures, we believe that this approach will provide great opportunity to optimize different functional materials to fulfill various electrochemical applications.
Figure 3. a) Discharge curves for Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] over the voltage range of 1.9–4.0 V versus Li$^+$/Li at different current densities. b) Ragone plot comparing the power and gravimetric energy densities based on the mass of Li$_7$[V$_{15}$O$_{36}$(CO$_3$)]. c) Cycle performance with Coulombic efficiency of Li$_7$[V$_{15}$O$_{36}$(CO$_3$)] at the high current density of 2 A g$^{-1}$ over 100 cycles.

Figure 4. The chronoamperometric response of the Li$_7$[V$_{15}$O$_{36}$(CO$_3$)]-based electrode by the potentiostatic intermittent titration techniques method (PITT). An expansion of the zone between 50 and 120 mA h g$^{-1}$ can be found in the Supporting Information (Figure S5).
Experimental Section

Synthesis of Li$_7$V$_{15}$O$_{36}$(CO$_3$) and Characterization: Li$_7$V$_{15}$O$_{36}$(CO$_3$) was prepared according to an adapted literature procedure. TGA-DTA was carried out on a Pyris Diamond TG-DTA (PE Co., USA) to obtain the optimized treatment temperature in a constant flow of dry N$_2$ (50 mL min$^{-1}$) and a heating/cooling rate of 10 °C min$^{-1}$. Alumina crucibles were loaded with 5–10 mg of sample powder. The weight loss before 200 °C (see Figure S2 in the Supporting Information) is ascribed to the dehydration of Li$_7$V$_{15}$O$_{36}$(CO$_3$)·nH$_2$O. The optimized treatment temperature was determined to be 200 °C and the samples were placed into a furnace to anneal at 200 °C for 10 h under N$_2$, and then were pulverized to a fine powder by ball milling after cooling to room temperature.

Cyclic voltammetry measurements were conducted on a CR2016-type coin cell. 1 M LiPF$_6$/ethylene carbonate (EC) dimethyl carbonate (DMC) ethyl methyl carbonate (EMC) (1:1:1, v/v) was used as the electrolyte. Cyclic voltammetry measurements were performed using a multichannel potentiostat (VMP2, Bio-logic Instruments). The authors thank Dr. De-Liang Long (University of Glasgow) for useful discussions. M.D.S. thanks the University of Glasgow for a Kelvin–Smith Research Fellowship and L.C. thanks the Royal Society for a Wolfson merit award.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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