**Improved Capacity Retention for LiVO$_2$ by Cr Substitution**

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We present a layered Li-intercalation oxide that operates on the V$^{3+}$/V$^{4+}$ redox couple. The stabilization effect of adding a +3 element into the layered LiVO$_2$ has been studied by first principles calculations. We identified Cr substitution into LiVO$_2$ to be promising for stabilizing a layered material based on the V redox couple. Layered LiCr$_x$V$_{1-x}$O$_2$ ($x = 0.1, 0.2, 0.4, 0.5$) has been synthesized and tested electrochemically. The improved capacity retention confirms that the structural stability of delithiated LiVO$_2$ is improved by Cr doping.

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Layered materials with the R-3m layered structure and composition LiMO$_2$ ($M =$ transition metals) have shown to be remarkably good as high energy density cathode materials for rechargeable batteries. LiCoO$_2$ is the original Li intercalation material from which the rechargeable Li battery industry grew. LiNiO$_2$ also has excellent Li cycling capability and Li mobility, but is not used in pure form due to its high oxidation character when delithiated. Among more recently developed cathode materials only those in the family of layered Li(Li, Ni, Co, Mn)O$_2$ have so far been able to offer improved energy density. It is therefore of interest to understand the potential of other layered compounds, and, if they do not reversibly intercalate, what their failure mode is. The most common failure modes are decomposition by reduction from the electrolyte or transition metal migration. The latter, for example, results in a layered to spinel transformation during charge and discharge.

**Methods**

**Computational.**— Computational results are derived from Density Functional Theory (DFT) calculations within the Generalized Gradient Approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) pseudo-potential as implemented in VASP.$^{20}$ A + $U$ correction term in the Dudarev scheme was used for V, Cr, Mn, Fe, Co and Ni. The exact $U$ values we used in this work were defined by Jain et al.$^{17}$ from fitting enthalpy of formation for binary oxides following the method by Wang et al.$^{21}$ All stability and voltage computations were performed using the aflow wrapper around VASP and the parameters proposed by Jain et al.$^{17,22}$

Stability computations for the different LiM$_x$V$_{1-x}$O$_2$ mixtures (with $M =$ Cr, Ti, Ga, Al, Fe, Ni, Mn, Co) were performed by choosing ten orderings of $M$ and $V$ using an enumeration algorithm proposed by Hart et al.$^{25}$ After DFT relaxation the total energy obtained for these mixtures was compared for stability at zero K to all known phases in the ICSD database as well as linear combinations of them using the convex hull construction. Computations obtained from GGA and GGA + $U$ are mixed following the scheme proposed by Jain et al.$^{23}$ For each compound, the energy for decomposition to more stable products, or “energy above the hull”, was evaluated. The energy above the hull is always non-negative. A large energy above the hull indicates a less stable compound. Stable phases at 0 K have an energy above the hull of 0 meV/atom.

**Experimental.**— LiCr$_x$V$_{1-x}$O$_2$ ($x = 0.1, 0.2, 0.4, 0.5$) samples were synthesized by solid-state reactions. Stoichiometric amounts of...
Table I. Oxidation states, stability and voltages for various layered LiM0.5V0.5O2.

<table>
<thead>
<tr>
<th>M in LiM0.5V0.5O2</th>
<th>Oxidation states</th>
<th>Energy above hull (meV/atom)</th>
<th>Voltage (V) LiM0.5V0.5O2→Li0.5M0.5V0.5O2</th>
<th>Voltage (V) Li0.5M0.5V0.5O2→M0.5V0.5O2</th>
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</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Ti4+ V2+</td>
<td>0</td>
<td>1.9</td>
<td>3.1</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr3+ V3+</td>
<td>3</td>
<td>2.7</td>
<td>3.6</td>
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<tr>
<td>Ga</td>
<td>Ga3+ V4+</td>
<td>7</td>
<td>2.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Al</td>
<td>Al3+ V3+</td>
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<td>Fe</td>
<td>Fe3+ V3+</td>
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<td>Ni</td>
<td>Ni4+ V4+</td>
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<td>Mn</td>
<td>Mn3+ V4+</td>
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<td>2.6</td>
<td>3.7</td>
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<tr>
<td>Co</td>
<td>Co3+ V4+</td>
<td>91</td>
<td>2.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

LiOH · H2O (98%, Alfa Aesar), Cr(OH)3(CH3COO)2 (Cr 24%, Alfa Aesar) and V2O5 (99.2%, Alfa Aesar) were mixed and half milled in aceton for 12 hours at a rate of 300 rpm. The mixture slurry was dried into a powder, and about 0.5 g of powder was pressed into a pellet. The pellet was fired at 800 °C in an argon flow for 12 hours before it was slowly cooled to room temperature.

Electrodes were fabricated using 60 wt% active material, 35 wt% super P carbon and 5 wt% PTFE as a binder, and tested in Swagelok cells using a 1 M LiPF6 in EC:DMC (1:1 in volume) as the electrolyte, and Li foil as the negative electrode. Swagelok cells were assembled in a glove box filled with argon, and galvanostatically charged and discharged at a rate of C/10 where 1C is theoretical capacity.

The in situ electrochemical cell consists of two aluminum plates measuring 4×4 cm2. Each has an 8 mm diameter hole at the center, which is covered by a Beryllium disk. The cathode foil, separator and Li foil are placed between the Beryllium windows. A rubber gasket is placed between two Al plates for sealing. The in situ X-ray diffraction patterns were collected on the beam line X16C at the National Synchrotron Light Source of Brookhaven National Laboratory. The wavelength of the X-ray source was 0.7027 Å. The full transmission diffraction patterns were recorded within minutes by using a strip detector that consists of 640 channels spanning a total angle of 8.704°.

Results

Using DFT computations, we investigated the energies of substituting various elements M for V in the layered structure. Table I shows stability in the lithiated state, voltage for delithiation and oxidation states for M = Cr, Ti, Ga, Al, Fe, Ni, Mn, and Co in LiM0.5V0.5O2. The stability at 0 K of the lithiated state is assessed by the convex hull construction. This procedure effectively compares the energy of a phase to all linear combination of competing phases, based on a database of calculated properties for all unique ICSD compounds. The energy above the hull indicates how far from stability a phase is. A compound with zero energy above hull is stable at 0 K. Based on known DFT errors, compounds with an energy above hull of under about 50 meV/atom also have a fair probability of being synthesizable. The table also indicates the oxidation state of vanadium and the element M. The oxidation states have been deduced from the magnetic moment present on the element at the completion of the DFT relaxation. Voltages for the first and second half of the capacity have also been computed.

According to the calculated results in Table I, the most stable mixture is between vanadium and Ti or Cr. However, Ti is oxidized to +4 while V is reduced to +2 when they are mixed. This is detrimental to the voltage that can be obtained from the material, as the first half of the capacity will correspond to the V5+/V4+ couple, resulting in a very low voltage of 1.9 V. The gallium and aluminium alloys are not as stable as Ti and Cr mixtures but are still within the range of possible DFT errors or within the range that can be stabilized by entropic factors. Moreover, the convex hull has been constructed using the 0 K ground state for LiGaO2 and LiAlO2 but at high temperature those two compounds are known to form layered structures. When the ground state structures are suppressed from the construction, we find that the Li0.5Ga0.5V0.5O2 and Li0.5Al0.5V0.5O2 are respectively only 6 meV/atom and 13 meV/atom above hull. This indicates that the two compounds are more favored energetically at high temperature. Considering its stability and voltage, we chose to investigate LiCr0.5V0.5O2 although we suspect that Ga and Al substituted systems may also be synthesizable.

In LiCr0.5V0.5O2, the average voltage at 2.7 V in the first half of the charge corresponds therefore to the V3+/V4+ couple, while the 3.6 V voltage is associated with the V4+/V5+ couple (Table I). The study of the calculated magnetic moments upon delithiation shows that Cr is inactive and stays +3. It is interesting to see that a similar capacity as for the pure LiVO2 compound (296 mAh/g) is still achievable when half of the active transition metal is replaced by an inactive element. This is due to the potential for two electron extraction exhibited by V3+. While delithiation of LiVO2 up to one Li per formula unit activates the +3 to +4 couple, LiCr0.5V0.5O2 can in principle also have one lithium per formula unit extracted by activating the +3 to +5 couple of V.

The large theoretical capacity available leads to attractive theoretical specific energy and energy density for LiCr0.5V0.5O2 (940 Wh/kg and 3781 Wh/l). These attractive energy densities are combined with a good thermal stability of the delithiated state. The safety of charged cathode materials is currently of great concern and can be related to the tendency for a cathode material to release oxygen upon heating. We recently developed a method to assess this tendency to release oxygen gas by computing the critical oxygen chemical potential for oxygen evolution. A high oxygen chemical potential will be associated with materials more easily releasing oxygen, and therefore more likely to be thermally unstable. Fig. 1 shows the computed oxygen chemical potential of the delithiated LiCr0.5V0.5O2 (in red) and compares it to a few known battery materials (in blue). In contrast to layered LiCoO2, LiCr0.5V0.5O2 is predicted to possess exceptional thermal stability. While the Co2O4 oxygen chemical potential is higher than 0 and therefore would thermodynamically release oxygen gas at 298 K in air, the vanadium based compound is closer to FePO4, one of the most thermally stable cathode materials.

Possible cation migration in layered Li0.5V2O5 and Li0.5Cr0.5V0.5O2 was investigated by computing the energy along the migration path from the transition metal layer to a site in the Li layer. Fig. 2a shows possible migration paths.

Figure 1. Critical oxygen chemical potentials for oxygen gas evolution for a few known charged cathodes (in blue) and for the half delithiated and fully delithiated LiCr0.5V0.5O2 (in red).
LiCoO$_2$ remains stable. As the migration barrier in LiVO$_2$ is sub-
high migration barrier, the migration of V or Cr is unlikely. Therefore,
demonstrates that LiMnO$_2$ and LiNi$_{2/3}$Sb$_{1/3}$O$_2$ will essentially
in Li$_{0.5}$VO$_2$ via the dumbell mechanism is very likely to occur. In
as
structure, and the energy barriers for both V and Cr migration are as high
configurations are about 0.6 eV higher than that of the layered struc-
ture, and the energy barriers for both V and Cr migration are as high
first charge, and becomes more sloping. Meanwhile, an additional
plateau around 4.1 V shows up, which is possibly attributed to the V$_3$
formation of V$_3$ trimers. Inspired by the computational results, we synthesized LiCr$_{x}$V$_{1-x}$O$_2$ ($x = 0.1, 0.2, 0.4, 0.5$) by solid-state reactions. X-ray diffraction
patterns in Fig. 3a show a single layered phase for the as-prepared
ions ($r_{\text{c}} = 0.615 \text{ Å}$) for a V$^{3+}$ ion ($r_{\text{V}} = 0.640 \text{ Å}$). The $a$ parameter,
however, anomalously increases with increasing Cr content. It is
known that vanadium atoms within the V plane of LiVO$_2$ cluster to
form V$_3$ trimers at room temperature. This clustering shrinks the
V-V distance, making the $a$ parameter of LiVO$_2$ significantly smaller
than that of LiCrO$_2$, even though the V$_3$ ion is larger than Cr$_3$.
Cr doping into the V plane increases the $a$ parameter by prohibiting the
formation of V$_3$ trimers.

Fig. 4 shows galvanostatic charge and discharge profiles of
LiCr$_{0.1}$V$_{0.9}$O$_2$ at C/10 at selected cycles. LiCr$_{0.1}$V$_{0.9}$O$_2$ shows a ca-
pacity of $\sim 120 \text{ mAh/g}$ for the first charge at the plateau around 2.8 V
which can be attributed to the V$^{3+}/V^{4+}$ redox couple. However, it
delivers only a capacity of $\sim 30 \text{ mAh/g}$ in the first discharge, and beh-
evies similarly to LiVO$_2$. In the following nine cycles, LiCr$_{0.1}$V$_{0.9}$O$_2$
largely retains its small capacity of $\sim 30 \text{ mAh/g}$. When the amount of
Cr is increased to 20%, the V$^{3+}/V^{4+}$ plateau is raised by $\sim 0.1 \text{ V}$ in the
first charge, and becomes more sloping. Meanwhile, an additional
plateau around 4.1 V shows up, which is possibly attributed to the
Cr$^{3+}/Cr^{4+}$ redox couple as the average voltage of Cr$^{3+}/Cr^{4+}$ couple in

our first principles calculations indicate that Cr substitution inhibits
ion migration in half delithiated LiCr$_{x}$V$_{1-x}$O$_2$ systems.

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patterns in Fig. 3a show a single layered phase for the as-prepared
LiCr$_{x}$V$_{1-x}$O$_2$ ($x = 0.1, 0.2, 0.4, 0.5$). Rietveld refinements with the
space group R-3m give a good fit for all the four compounds. Lattice
constants from the refinements are shown in Fig. 3b. The lattice
constant $a$ increases while $c$ decreases with Cr doping, which is con-
sistent with the results obtained by Goodenough et al.$^{38}$ The decrease
of $c$ parameter is expected with the substitution of a smaller Cr$^{3+}$
ion ($r_{\text{C}} = 0.615 \text{ Å}$) for a V$^{3+}$ ion ($r_{\text{V}} = 0.640 \text{ Å}$). The $a$ parameter,
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plateau around 4.1 V shows up, which is possibly attributed to the
Cr$^{3+}/Cr^{4+}$ redox couple as the average voltage of Cr$^{3+}/Cr^{4+}$ couple in

the formation of the Li/M dumbbell configuration. The first step in
Li/M dumbbell formation is the creation of a trivacancy in the Li layer,
followed by migration of the M from the octahedral site into the face-
shar in the Li layer. Meanwhile, one Li moves to the
tetrahedral site on the other side of the now vacant M-site. The
details of the formation of a Li/M dumbbell configuration can also be
found in our previous papers.$^{9,19}$

Fig. 2b compares the energy barriers of ion migration in half
delithiated LiVO$_2$ and LiCr$_{0.5}$V$_{0.5}$O$_2$. Forming a Li/V dumbbell config-
furation in Li$_{0.5}$VO$_2$ lowers the energy by 0.11 eV, indicating that the
Li/V dumbbell configuration is preferred thermodynamically. The energy
barrier for the V migration is 0.78 eV. Previous work has shown energy
barriers in partial delithiated LiMnO$_2$ ($\sim 0.4$ eV), LiCoO$_2$ ($\sim 1.6$ eV) and LiNi$_{2/3}$Sb$_{1/3}$O$_2$ ($\sim 0.6$ eV).$^{9,19}$ Experimental evidence
demonstrates that LiMnO$_2$ and LiNi$_{2/3}$Sb$_{1/3}$O$_2$ will essentially
transform into a spinel type structure, while the layered structure of
LiCoO$_2$ remains stable.$^{9,19}$ As the migration barrier in LiVO$_2$ is sub-
stantially closer to that in LiMnO$_2$ and LiNi$_{2/3}$Sb$_{1/3}$O$_2$, V migration
in Li$_{0.5}$VO$_2$ via the dumbbell mechanism is very likely to occur. In
Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$, however, energies of both Li/V and Li/Cr dumbbell
configurations are about 0.6 eV higher than that of the layered struc-
ture, and the energy barriers for both V and Cr migration are as high
as $\sim 1.5$ eV, very close to that of Co migration in LiCoO$_2$. With this
high migration barrier, the migration of V or Cr is unlikely. Therefore,
layered LiCrO\textsubscript{2} was calculated to be about 4.11 V.\textsuperscript{40} The first discharge of all samples with 20\% or more Cr is significantly better than that of 10\% Cr sample, with the discharge capacity reaching 150 mAh/g. For the second charge, LiCr\textsubscript{0.2}V\textsubscript{0.8}O\textsubscript{2} shows a capacity of 150 – 160 mAh/g, and the two plateaus around 2.8 V and 4.1 V become less distinct. After ten cycles, the discharge capacity of LiCr\textsubscript{0.2}V\textsubscript{0.8}O\textsubscript{2} drops to 115 mAh/g. When the Cr content increases up to 40\% and 50\%, the electrochemical behavior is very similar to that of LiCr\textsubscript{0.2}V\textsubscript{0.8}O\textsubscript{2}.

Fig. 5a shows the full transmission XRD patterns for LiCr\textsubscript{0.5}V\textsubscript{0.5}O\textsubscript{2} at various stages of its first charge and discharge.\textsuperscript{20} has been converted to that for the wavelength of Cu K\textsubscript{\alpha}. The broad peaks and backgrounds are from cell components such as separators, carbon and binders, etc. The doublet peaks around 71° is from the (102) diffraction of Beryllium disks on two sides of the in situ cell. Most peaks from the active material LiCr\textsubscript{0.5}V\textsubscript{0.5}O\textsubscript{2} shift in angle during charge and discharge, and the (018) diffraction disappears or merges with the (110) diffraction as shown in Fig. 5c. Fig. 5b shows an additional peak that appears closely below the (003) diffraction during the charge process, and remains until the end of discharge.

**Discussion**

Our first principles calculations demonstrate that the partial substitution of V with Cr increases the V\textsuperscript{3+} migration barrier by 0.67 eV, and additionally makes Li/V dumbell formation thermodynamically unstable. To understand the effect of Cr on the migration barrier, we investigated the oxidation states along the migration paths\textsuperscript{9} (shown in Table II). In Li\textsubscript{0.5}VO\textsubscript{2}, the migrating V is in a +3 oxidation state at all three positions (octahedral, octahedral/tetrahedral face, and tetrahedral). In Li\textsubscript{0.5}Cr\textsubscript{0.5}V\textsubscript{0.5}O\textsubscript{2}, however, all V have been oxidized to +4. When one V\textsuperscript{4+} migrates to the tetrahedral site, it reduces to V\textsuperscript{3+}. Meanwhile, one of its nearest neighboring V\textsuperscript{4+} is oxidized into V\textsuperscript{5+}. The charge disproportionation can be written as 2V\textsuperscript{4+} (oct) \rightarrow V\textsuperscript{3+} (tet) + V\textsuperscript{5+} (oct). It is known that V\textsuperscript{5+} is energetically more stable in tetrahedral\textsuperscript{41} or trigonal bipyramid\textsuperscript{42} sites due to its electronic configuration and small ionic size. The creation of V\textsuperscript{5+} in an octa-
Table II. Oxidation states of the migrating ions at different positions.

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<tr>
<th>Migration ions</th>
<th>Octahedral oxidation state</th>
<th>Octa/Tetra face oxidation state</th>
<th>Tetrahedral oxidation state</th>
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<tbody>
<tr>
<td>V in Li0.5VO2</td>
<td>3</td>
<td>3</td>
<td>3</td>
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<tr>
<td>V in Li0.5Cr0.5V0.5O2</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cr in Li0.5Cr0.5V0.5O2</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cr in Li0.5Cr0.5O2</td>
<td>3</td>
<td>3.4</td>
<td>3.7</td>
</tr>
</tbody>
</table>

dral site by the reduction of the migration V\(^{+3}\) (oct) to V\(^{+1}\) (tet) may be what is responsible for the high migration barrier in Li0.5Cr0.5V0.5O2.

Our hypothesis based on oxidation state analysis suggests that V migration requires both a migrating V in the +3 oxidation state and Li trivacancies. Before LiCr0.5V0.5O2 is half delithiated, there are indeed V\(^{+3}\) available. However, significant V migration might not occur because a low concentration of Li vacancies in the early stage of the charge will result in very low concentration of trivacancies in the Li layer. When the Cr doping rate is very low (such as 10%), there are still significant amount of V\(^{+3}\) available when LiCr\(_{1-x}\),\(_{x}\)O\(_{2}\) is half delithiated. Thus, the V\(^{+3}\) can migrate into tetrahedral sites without forming V\(^{+4}\) in octahedral sites. To prevent octahedral V\(^{+3}\) formation to the point that it improves capacity, a higher amount of Cr doping, e.g. 20% or more, seems necessary. Hence, while V ions migrate isovalently as V\(^{+3}\) in LiVO\(_{2}\), it is the oxidation enhanced migration of V in LiCr\(_{0.5}\)V\(_{0.5}\)O\(_{2}\) that makes its migration more difficult.

The Cr migration barrier in Li\(_{1-x}\)Cr\(_{x}\)V\(_{0.5}\)O\(_{2}\) is about 0.22 eV higher than in Li\(_{1-x}\)Cr\(_{x}\)O\(_{2}\), as is shown in Fig. 2b. In Li\(_{1-x}\)Cr\(_{x}\)O\(_{2}\), the Cr are +3 and half are +4. The migrating Cr starts with a valence state of +3 but is oxidized to +3.7 on the migrating path as is shown in Table II. Meanwhile, one Cr\(^{+4}\) close to the migrating Cr ion obtains one electron, being reduced to Cr\(^{+3}\). In Li\(_{1-x}\)Cr\(_{x}\)V\(_{0.5}\)O\(_{2}\), however, all Cr stays in the +3 state during migration. The migration barrier of Cr in Li\(_{1-x}\)Cr\(_{x}\)V\(_{0.5}\)O\(_{2}\) is about 0.22 eV higher than that in Li\(_{1-x}\)Cr\(_{x}\)O\(_{2}\), suggesting that Cr\(^{+3}\) is less mobile than Cr\(^{+4}\). In Li\(_{1-x}\)Cr\(_{x}\)V\(_{0.5}\)O\(_{2}\), however, the relatively more mobile Cr\(^{+4}\) cannot be formed through any possible charge disproportionation of V\(^{+4}\) and Cr\(^{+3}\).

Our computational results indicate that V\(^{+3}\) (tet) is more stable than V\(^{+4}\) (tet), while Cr\(^{+4}\) (tet) is more stable than Cr\(^{+3}\) (tet), which is why Cr\(^{+3}\) needs to be oxidized while migrating, while V\(^{+4}\) needs to be reduced to migrate. This site preference can be explained based on the electronic states of the 3d electrons. Fig. 6 shows schematically the relative position of 3d states in the relevant sites, 3.4 When Cr\(^{+4}\) migrates from an octahedral (Oh) to a tetrahedral (Td) site, two 3d electrons are rearranged from t\(_{2g}\) orbitals of Oh to the e orbitals of Td. As the two e orbitals are split off from the t\(_{2g}\) orbitals in the tetrahedral symmetry by a gap, Cr\(^{+4}\) (oct) is energetically preferred. With a similar analysis, it can be found that V\(^{+3}\) (tet) is energetically preferred while V\(^{+4}\) (tet) is not.

Although the measured capacity was significantly improved by substituting more than 20% Cr into LiVO\(_{2}\), the in situ XRD results suggest that some structural change still occurs during charge and discharge. Fig. 5b shows one peak around 18° belonging to the (003) diffraction. During the charge process, the (003) diffraction shifts to a higher angle indicating a decrease of the c lattice parameter. Meanwhile, as the two e orbitals are split off from the t\(_{2g}\) orbitals in the tetrahedral symmetry by a gap, Cr\(^{+4}\) (oct) is energetically preferred. With a similar analysis, it can be found that V\(^{+3}\) (tet) is energetically preferred while V\(^{+4}\) (tet) is not.

Figure 6. Schematic 3d electron structures of Cr\(^{+3}\) and V\(^{+3}\) in octahedral (Oh) and tetrahedral (Td) sites. The Cr\(^{+4}\)/V\(^{+5}\) is formed by removing the top electron of Cr\(^{+3}\)/V\(^{+4}\).

Conclusions

First principles calculations indicated that Cr substitution into LiVO\(_{2}\) can significantly increase the V migration barrier upon partial charge, and improve the structural stability with respect to Li/V dumbbell formation. Electrochemical results of LiCr\(_{0.5}\)V\(_{0.5}\)O\(_{2}\) show improved capacity, confirming the computational prediction. However, we still detect minor structural transformations that are yet to be fully understood. Further study of +3 metal doping into LiVO\(_{2}\) might result in additional insights and better electrochemical performance.
Acknowledgment

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