Improved Capacity Retention for LiVO$_2$ by Cr Substitution

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1149/2.046302jes">http://dx.doi.org/10.1149/2.046302jes</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>Electrochemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Accessed</td>
<td>Thu Mar 07 23:09:01 EST 2019</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/82519">http://hdl.handle.net/1721.1/82519</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher’s policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td></td>
</tr>
</tbody>
</table>
Improved Capacity Retention for LiVO₂ by Cr Substitution

Xiaohua Ma, Geoffrey Hautier, Anubhav Jain, Robert Doe, and Gerbrand Ceder

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

We present a layered Li-intercalation oxide that operates on the V³⁺/V⁴⁺ redox couple. The stabilization effect of adding a +3 element into the layered LiVO₂ has been studied by first principles calculations. We identified Cr substitution into LiVO₂ to be promising for stabilizing a layered material based on the V redox couple. Layered LiCrₓV₁₋ₓO₂ (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 LiVO₂ is improved by Cr doping.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.046302jes] All rights reserved.
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>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Ti³⁺, 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>
</tr>
<tr>
<td>Ga</td>
<td>Ga³⁺, V⁴⁺</td>
<td>17</td>
<td>2.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Al</td>
<td>Al³⁺, V³⁺</td>
<td>22</td>
<td>2.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe³⁺, V³⁺</td>
<td>48</td>
<td>2.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni²⁺, V⁴⁺</td>
<td>47</td>
<td>3.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn³⁺, V⁴⁺</td>
<td>77</td>
<td>2.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Co</td>
<td>Co²⁺, V⁴⁺</td>
<td>91</td>
<td>2.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

LiOH·H₂O (98%, Alfa Aesar), Cr₃(OH)₆(CH₃COO)₇·H₂O (Cr 24%, Alfa Aesar) and V₂O₅ (99.2%, Alfa Aesar) were mixed and ball 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 1 M LiPF₆ in EC:DMC (1:1 in volume) as the electrolyte, super P carbon and 5 wt% PTFE as a binder, and tested in Swagelok cells using 1 M LiPF₆ in EC:DMC (1:1 in volume) as the electrolyte, 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.³⁷ ³⁸ 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,³¹ 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 aluminum 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 V⁵⁺/V⁴⁺ couple, while the 3.6 V voltage is associated with the V⁴⁺/V³⁺ 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 V⁴⁺. 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.³² ³³ 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.²⁹ Fig. 1 shows the computed oxygen chemical potential of the delithiated LiCr₀.₅V₀.₅O₂ (in red) and compared 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 Co₂O₃ 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.³⁴ ³⁵ Possible cation migration in layered LiₓV₂O₅ and LiₓCr₀.₅V₀.₅O₂ 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

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
as configuration, 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-
transform into a spinel type structure, while the layered structure of
1.6 eV) and LiNi$_{2/3}$Sb$_{1/3}$O$_2$ ($\sim$0.6 eV). Experimental evi-
dicts that LiMnO$_2$ and LiNi$_{2/3}$Sb$_{1/3}$O$_2$ will essentially
spinel type structure, while the layered structure of
Li/M dumbell formation is the creation of a trivacancy in the Li layer,
forming a Li/V dumbbell configuration. The first step in
Li/M dumbell configuration is the creation of a trivacancy in the Li layer,
followed by migration of the M from the octahedral site into the face-
sharing tetrahedral site 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$_{0.1}$V$_{0.9}$O$_2$. Forming a Li/V dumbbell
configuration 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 structure, 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$. With this
high migration barrier, the migration of V or Cr is unlikely. Therefore,
our first principles calculations indicate that Cr substitution inhibits ion migration in half delithiated LiCr$_x$V$_{1-x}$O$_2$ systems.

Inspired by the computational results, we synthesized LiCr$_{0.1}$V$_{0.9}$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 LiCr$_{0.1}$V$_{0.9}$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 consistent 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 ($r_C = 0.615$ Å) for a V$^{3+}$ ion ($r_V = 0.640$ 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.39 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.38

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-

capacity of $\sim$120 mAh/g for the first charge at the plateau around 2.8 V
which can be attributed to the V$^{3+}$/V$^{4+}$ redox couple.31 However, it delivers only a capacity of $\sim$30 mAh/g in the first discharge, and behaves similarly to LiVO$_2$.13 In the following nine cycles, LiCr$_{0.1}$V$_{0.9}$O$_2$ largely retains its small capacity of $\sim$30 mAh/g. When the amount of Cr is increased to 20%, the V$^{4+}$/V$^{3+}$ plateau is raised by $\sim$0.1 V in the first charge, and becomes more sloping. Meanwhile, an additional plateau around 4.1 V shows up, which is possibly attributed to the Cr$^{3+}$/Cr$^{4+}$ redox couple as the average voltage of Cr$^{3+}$/Cr$^{4+}$ couple in
layered LiCrO$_2$ was calculated to be about 4.11 V. 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$_{0.2}$V$_{0.8}$O$_2$ 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$_{0.2}$V$_{0.8}$O$_2$ 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$_{0.2}$V$_{0.8}$O$_2$.

Fig. 5a shows the full transmission XRD patterns for LiCr$_{0.5}$V$_{0.5}$O$_2$ at various stages of its first charge and discharge. $2\theta$ has been converted to that for the wavelength of Cu K$_\alpha$. The broad peaks and backgrounds are from cell components such as separators, carbon and binders, etc. The doublet peaks around 71$^\circ$ is from the (102) diffraction of Beryllium disks on two sides of the in situ cell. Most peaks from the active material LiCr$_{0.5}$V$_{0.5}$O$_2$ 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 $V^{3+}$ 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 (shown in Table II). In Li$_{0.5}$VO$_2$, the migrating V is in a +3 oxidation state at all three positions (octahedral, octahedral/tetrahedral face, and tetrahedral). In Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$, however, all V have been oxidized to +4. When one $V^{4+}$ migrates to the tetrahedral site, it reduces to $V^{3+}$. Meanwhile, one of its nearest neighboring $V^{4+}$ is oxidized into $V^{5+}$. The charge disproportionation can be written as $2V^{4+}$ (oct) $\rightarrow$ $V^{3+}$ (tet) + $V^{5+}$ (oct). It is known that $V^{5+}$ is energetically more stable in tetrahedral or trigonal bipyramidal sites due to its electronic configuration and small ionic size. The creation of $V^{5+}$ in an octahedral...
Table II. Oxidation states of the migrating ions at different positions.

<table>
<thead>
<tr>
<th>Migration ions</th>
<th>Octahedral oxidation state</th>
<th>Octa/Tetra face oxidation state</th>
<th>Tetrahedral oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>V in Li$_{0.5}$VO$_2$</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>V in Li$<em>{0.5}$Cr$</em>{0.5}$VO$_2$</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cr in Li$<em>{0.5}$Cr$</em>{0.5}$VO$_2$</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cr in Li$<em>{0.5}$Cr$</em>{0.5}$O$_2$</td>
<td>3</td>
<td>3.4</td>
<td>3.7</td>
</tr>
</tbody>
</table>

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 LiCr$_{0.5}$V$_{0.5}$O$_2$ 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$_3$V$_1$O$_2$ is half delithiated. Thus, the V$^{3+}$ can migrate into octahedral 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 Li$_2$VO$_2$, it is the oxidation enhanced migration of V in Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$ that makes its migration more difficult.

The Cr migration barrier in Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$ is about 0.22 eV higher than in Li$_{0.5}$CrO$_2$, as is shown in Fig. 2b. In Li$_{0.5}$CrO$_2$, half the Cr are +3 and half are +4. The migrating Cr starts with a valence state of +3 but is oxidized to +4 on the migrating path as is shown in Table II. Meanwhile, one Cr$^{4+}$ close to the migrating Cr ion obtains an electron, being reduced to Cr$^{3+}$. In Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$, however, all Cr stays in the +3 state during migration. The migration barrier of Cr in Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$ is about 0.22 eV higher than that in Li$_{0.5}$CrO$_2$, suggesting that Cr$^{3+}$ is more stable than Cr$^{4+}$. In Li$_{0.5}$Cr$_{0.5}$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$^{4+}$ (oct), 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 3$d$ electrons. Fig. 6 shows schematically the relative position of 3$d$ states in the relevant sites.41,43 When Cr$^{4+}$ migrates from an octahedral ($O_h$) to a tetrahedral ($T_d$) site, two 3$d$ electrons are rearranged from $t_2$ orbitals of $O_h$ to the $e$ orbitals of $T_d$. As the two $e$ orbitals are split off from the $t_2$ 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 Li$_2$VO$_2$, 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 higher angle indicating a decrease of the $c$ lattice parameter. Meanwhile, an additional peak occurs below the (003) diffraction, which could be due to the (111) diffraction of a spinel-like structure.44 In Fig. 5c, the adjacent (018) and (110) diffractions, which are defining characteristics of the layered structure, merge into one diffraction peak. It is possible that the two diffractions merge into one (440) diffraction of a spinel-like structure.45,46 However, most other diffractions belonging to the layered structure, such as (003), have not changed significantly, implying that the structural transformation, if any, happens only partially. During the discharge process, the additional peak below the (003) diffraction remains, and the adjacent (018) and (110) diffractions are not recovered, indicating that the structural transformation is not reversible. However, results from first principles calculations suggest that the structural transformation through the formation of Li/Cl or Li/V dumbbell configuration is unlikely at x<0.5 in Li$_{0.5}$Cr$_{0.5}$V$_{0.5}$O$_2$. It is however possible that some V migration occurs for x>0.5 when V$^{3+}$ is still present. While the trivacancy concentration will be smaller for x<0.5 it is nonetheless non-zero, and may lead to slow V$^{3+}$ migration.

The 2.8 V plateau during first charge in Fig. 4a is very close to our calculated voltage of 2.7 V, which is attributed to the V$^{3+}$/V$^{4+}$ redox couple. It also agrees with electrochemical results of layered LiVO$_2$.13,14 The consistency between the calculated and experimental voltages also indicates that no structural transformation occurs during the early stage of the charge, which is consistent with the in situ XRD results. The 4.1 V plateau of LiCr$_{0.5}$V$_{1.5}$O$_2$ (x = 0.2, 0.4, 0.5) in Fig. 4a is about 0.5 V higher than the calculated V$^{4+}$/V$^{3+}$ redox couple. The calculated 3.6 V for V$^{3+}$/V$^{4+}$ assumes a perfect layered structure all through the charge process. The structural transformation shown in the in situ XRD may modify the V$^{4+}$/V$^{3+}$ voltage. As is indicated by in situ XRD, spinel-like structures form partially with Li or V in the tetrahedral sites, which will block the Li diffusion paths significantly. It is possible that tetrahedral Li needs to be extracted before octahedral Li can be taken out, which could result in a higher voltage. We have tried to clarify the origin of the 4.1 V plateau by XPS analysis. However, the results turned out to be inconclusive due to the conjugation of oxidation state change and structural transformation.

**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$_{1.5}$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.

---

**Figure 6.** Schematic 3$d$ electron structures of Cr$^{3+}$ and V$^{3+}$ in octahedral ($O_h$) and tetrahedral ($T_d$) sites. The Cr$^{4+}$/V$^{3+}$ is formed by removing the top electron of Cr$^{3+}$/V$^{3+}$.
Acknowledgment

This work was supported by the Robert Bosch Co. and by Umicore. The authors thank Dr. Hailong Chen and Prof. Peter Stephens for help with the in situ XRD.

References