The magnetic moment of the half-metallic ferromagnetic oxide CrO$_2$ has been modified via electrochemical lithiation. In the low-Li regime, below about $x = 0.2$ in Li$_x$CrO$_2$, a large change in magnetization of 20 ± 2% per 0.1 Li/formula unit is obtained, in reasonable agreement with a model based on the change in oxidation state of the Cr ions. The change in magnetization is partly reversible, especially for $x \leq 0.1$. The kinetics and reversibility of the process are improved at 60°C, and Li contents up to $x = 0.9$ could be inserted. At these concentrations the room-temperature moment is reduced to <5% of its initial value. This decrease is irreversible, due to disruption of the rutile crystal structure of the CrO$_2$.

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Electrochemical insertion of Li into CrO$_2$ at room temperature.—Room-temperature lithiation of CrO$_2$ led to a decrease in the saturation magnetization of up to 70% (Fig. 2). A maximum of 0.5 mol Li per formula unit of CrO$_2$ ($x = 0.5$) could be inserted at room temperature during the electrochemical discharge process. The changes in magnetic moment correlate with structural changes apparent from XRD measurements. The CrO$_2$ (101) rutile-structure peak broadens for $x = 0.1$, and shoulder peaks appear at lower angles for $x = 0.4$ and 0.5 (Fig. 3). This suggests an inhomogeneous

slope subtraction procedure had only a small effect (~3 to 4%) on the calculated change in saturation magnetization caused by lithiation.

X-ray diffraction (XRD) of opened cells was carried out in $\theta$–$2\theta$ geometry using a diffractometer with Cu $K\alpha$ radiation. The starting powders contain some trace Cr$_2$O$_3$ estimated to be $<1\%$ from the ratio of XRD peak intensities. The CrO$_2$ phase may decompose upon exposure to the atmosphere because it is metastable at ambient conditions. This was evident in some samples that were exposed to the atmosphere for a prolonged period after overnight vacuum drying at 120°C, in which XRD peaks corresponding to the orthorhombic oxyhydroxide CrO(OH) phase were found. In order to avoid unwanted reactions, the cathodes were stored and assembled into coin cells inside a glove box prior to the experiments.

Results and Discussion

Figure 2. Magnetic hysteresis loops for Li$_x$CrO$_2$ with different Li contents $x$ normalized to the magnetization of pristine CrO$_2$.

Figure 3. Upper panels: Comparison of (a) (110), (b) (101), and (c) (211) X-ray peaks for samples discharged to different lithium contents $x = 0.1$, 0.4, and 0.5 at 20°C, compared to the peak from the pristine CrO$_2$ sample. All peaks are shown with the same vertical scale. Lower panels: (a) (110), (b) (101), and (c) (211) peaks for samples after several discharge–charge cycles. All peaks are shown at the same scale as the peaks in the pristine sample.
The reversibility of the Li insertion was examined by discharging and charging the samples up to four times. Figure 4 shows the discharge–charge curves for $x = 0$. This discharge–charge cycle was repeated up to four times, indicating that there is some structural degradation. For $x = 0.1$, there is reasonably good electrochemical reversibility. The sample for $x = 0.3$ shows poor electrochemical reversibility and in this case, the discharge capacity is higher than charging capacity.

Figure 4. Charge and discharge cycles of CrO$_2$ samples at a current of 3.2 mA/g at room temperature showing the variation of cell voltage $E$ with charge flow $Q$: (a) $x = 0.1$, (b) $x = 0.2$, and (c) $x = 0.3$, where $x$ represents the maximum Li content inserted into each sample. The samples were cycled four times.

Electrochemical reversibility of LixCrO$_2$ at room temperature.— The reversibility of the Li insertion was examined by discharging samples (inserting Li) up to different values of $x$ and then charging the samples (removing Li) to return to a nominal composition of $x = 0$. This discharge–charge cycle was repeated up to four times. Figure 4 shows the discharge–charge curves for $x = 0.1$, $0.2$, and $0.3$. The system shows near-perfect electrochemical reversibility at $x = 0.1$, but a decrease in final voltage is observed upon cycling, which suggests that there is some structural degradation. For $x = 0.2$, there is reasonably good electrochemical reversibility. The sample for $x = 0.3$ shows poor electrochemical reversibility and in this case, the discharge capacity is higher than charging capacity.

The corresponding structural changes are indicated in Fig. 3 (lower panels). As noted above, Li insertion lowers the CrO$_2$ peak intensity, broadens the peaks, shifts them to lower angles, and introduces additional low-angle shoulders at $x = 0.3$ or higher. Li removal partly reverses these changes and results in an X-ray pattern close to that of the pristine powder, even for $x = 0.3$. For example, a sample discharged to $x = 0.3$ shows a shoulder peak adjacent to the broadened (101) peak, but after cycling four times between $x = 0$ and 0.3 and returning to $x = 0$, the shoulder peak is absent. The peak broadening is not fully reversible, for example, the sample cycled four times to $x = 0.3$ has a full width at half maximum for the (101) peak of 0.49°, compared to 0.33° for the pristine powder and 0.84° for the discharged state. These results suggest that Li insertion creates some irreversible inhomogeneous strain in the lattice. Furthermore, the $a$-axis lattice parameter, as calculated from the shoulder peak observed for Li$_{0.1}$CrO$_2$ (110), is $\sim 4.55$ Å. This is 3% longer than the $a$-axis lattice parameter of the pristine CrO$_2$ phase. This expansion is consistent with the 9.5% increase observed for the $a$-axis lattice parameter in Li$_{0.5}$CrO$_2$ prepared by chemical lithiation. However, the peak broadening observed in our samples makes a more detailed comparison difficult, particularly for higher lithium contents.

Intermittent discharge measurements (Fig. 5) supported the XRD observations. In these measurements, Li insertion is periodically interrupted by zero-current periods of relaxation lasting 5 h each. The open-circuit voltages (OCV) observed after 5 h of relaxation decrease as a function of $x$ in Li$_x$CrO$_2$ with a relatively small polarization ($\sim 200$ mV) in the low-$x$ limit. Also, a much larger slope in the OCV $x$-curve was observed for $x < 0.05$ than for higher lithium contents. This is consistent with the existence of a predominantly single phase at low $x$, as suggested by XRD. The significantly large polarization ($\sim 1000$ mV) in the region $x > 0.2$ may indicate a change in the nature of the lithiation reaction at higher Li contents.

Figure 5. Intermittent charge curves of a CrO$_2$ sample at a rate of 3.2 mA/g at room temperature. The sample was charged multiple times, each one separated by a 5 h off period. Open circles indicate the OCVs measured after each 5 h current-off period.

Figure 6 shows the magnetization as a function of Li content for room temperature involving a topochemical reaction mechanism. The open-circuit voltages (OCVs) observed after 5 h of relaxation decrease as a function of $x$ in Li$_x$CrO$_2$ with a relatively small polarization ($\sim 200$ mV) in the low-$x$ limit. Also, a much larger slope in the OCV $x$-curve was observed for $x < 0.05$ than for higher lithium contents. This is consistent with the existence of a predominantly single phase at low $x$, as suggested by XRD. The significantly large polarization ($\sim 1000$ mV) in the region $x > 0.2$ may indicate a change in the nature of the lithiation reaction at higher Li contents.

Figure 6 shows the magnetization as a function of Li content for different numbers of discharge–charge cycles. Even for $x = 0.1$, a single complete discharge–charge cycle leads to a drop in magnetization of 15% (Fig. 7). Although the process is electrochemically reversible up to $x = 0.1$, the magnetization is not reversible to the same extent. A larger drop in magnetization was obtained for three discharge–charge cycles (Fig. 6), indicating that electrochemical cy-
cling leads to progressively higher structural degradation. The irreversibility is more pronounced for higher $x$, where little of the magnetic moment is recovered upon removing the Li from the structure.

**Electrochemical cycling of Li$_x$CrO$_2$ at 60°C.**—As mentioned above, the kinetics in this system are poor at room temperature, as is evident from the large polarization obtained upon electrochemical cycling. Improvement in the kinetics of lithiation may be expected to increase the amount of lithium that can be inserted and the reversibility of the structural and magnetic changes. To improve the kinetics, samples were subjected to 1–2 electrochemical cycles at 60°C in which Li amounts varying between $x = 0.5$ and 0.9 were inserted. Li insertion beyond $x = 0.9$ was limited by the cell, reaching the voltage cutoff of 0.9 V. In Fig. 8, the discharge–charge curves at room temperature and at 60°C are plotted for comparison. There is less polarization at 60°C, implying a reduced kinetic limitation and enabling insertion of more Li than is possible at room temperature.

Structurally, cycling at 60°C also leads to broadening of the peak and development of a shoulder peak at $x = 0.5$ (Fig. 9), which decreases in intensity but does not fully disappear upon charging back to the unlithiated state. At $x = 0.75$ and 0.9, however, the shoulder peak is retained upon charging back to $x = 0$. The broadening of the (101) peak indicates that there is progressive destruction of long-range order in the rutile lattice, and the broadening becomes increasingly irreversible beyond $x = 0.5$.

The resultant changes in magnetization with Li content at 60°C are superposed on Fig. 6. The magnetization is <5% of its initial value at room temperature but increases to 10% at 60°C for $x = 0.2$. This suggests that the structural degradation is more pronounced at lower temperatures, consistent with the decrease in polarization observed in Fig. 8.

**Figure 6.** Summary of magnetization measurements of CrO$_2$ after electrochemical cycling. The samples were subjected to different numbers of discharge–charge cycles and left in the discharged (lithiated) state or the charged (delithiated) state. The solid points indicate room-temperature data while the open points refer to 60°C measurements. For example, “20°C 3.5 cycles, lithiated” refers to a sample that has been subjected to three discharge–charge cycles at 20°C, followed by a discharge to leave it at composition $x$. The shaded area of the graph indicates complete electrochemical reversibility. The line from $x = 0$ to $x = 0.2$ represents the predictions of a model based on the change in the Cr valence state upon lithiation, for samples discharged once (A).

**Figure 7.** Comparison of magnetic properties before lithiation (■), after insertion of $x = 0.1$ mol Li (▲), and after removing Li (charging) back to $x = 0$ (▲).
value when the lithium content reaches \( x = 0.75 \). However, the reversibility of the change in magnetization is still quite limited, and the electrochemical reversibility evident in the charge–discharge curves, which extends until at least \( x = 0.5 \) at 60°C, is not matched by the reversibility of the magnetization.

The \( M_s(x) \) behavior in the range \( x = 0.2–1 \) is approximately linear (Fig. 6). A possible explanation for this is the presence of two rutile-structure phases, as suggested by the XRD data above \( x = 0.2 \): one magnetic and the other with no net moment. This is also supported by the intermittent discharge measurement that suggests two different Li insertion mechanisms in the low and intermediate \( x \)-regimes (Fig. 5). The change in the voltage across the sample during the 5 h relaxation period is modest (\( \sim -200 \text{ mV} \)) for \( x < 0.1 \) but increases to \(-1 \text{ V} \) for larger \( x \), indicating a change in the kinetics of the Li insertion.

**Modeling.**—To analyze the effects of Li insertion on the magnetization, we assume that the rutile framework is retained upon lithiation. There are three possible interactions between \( t_2g \) orbitals, namely, \( e_g-e_g, t_{2g}-t_{2g}, \) and \( e_g-t_{2g} \). We consider the \( t_{2g}-t_{2g} \) interactions alone, because the \( e_x \) orbitals are empty. In \( \text{CrO}_2 \), the degeneracy of the \( t_{2g} \) states is lifted due to tetragonal symmetry. As a result, there exist \( d_{x^2} + d_{y^2} \) and \( d_{x^2} + d_{y^2} \) degenerate excited states above the \( d_{z^2} \) ground state. Therefore each \( \text{Cr}^{4+} \) ion in the lattice has one localized electron in \( d_{z^2} \), and an itinerant electron that has equal probability of occupying each of the excited states.

The source of the ferromagnetism is the parallel coupling of spins due to hopping of the itinerant electron between neighboring \( \text{Cr}^{4+} \) (\( d^5 \)) ions. We assume that insertion of a \( \text{Li}^{+} \) ion leads to reduction of a \( \text{Cr}^{4+} \) ion (moment 2\( \mu_B \)) into a \( \text{Cr}^{3+} \) ion (3\( \mu_B \)) for charge balance, and that there is no competing charge compensating mechanism, such as the filling of oxygen vacancies. The reduction of \( \text{Cr}^{4+} \) to \( \text{Cr}^{3+} \) creates \( d^2-d^2 \) and \( d^3-d^3 \) nearest-neighbor pairs, which leads to antiparallel coupling of spins through superexchange interaction between the \( t_{2g} \) orbitals. This is because interactions between half-filled orbitals are antiferromagnetic in nature due to Pauli’s exclusion principle and the conservation of spin upon electron transfer.

At low Li concentrations, one can assume that \( d^2-d^2 \) and \( d^3-d^3 \) are the dominant interactions. This gives a ground state wherein the \( \text{Cr}^{4+} \) ions are coupled parallel to each other and are coupled antiparallel to the small number of \( \text{Cr}^{3+} \) ions present. Neglecting the parallel coupling between neighboring \( \text{Cr}^{3+} \) ions, because such pairs would be present in very small concentrations, we expect a decrease in magnetic moment of \( 5\mu_B \) for each \( \text{Cr}^{4+} \) ion that is incorporated into the structure. This corresponds to a change in moment of 1629 emu/cm\(^3\) at 0 K, or equivalently, a 250% decrease in magnetization, for each mole of \( \text{Li} \) per formula unit of \( \text{CrO}_2 \). A line with this slope is shown in Fig. 6, and is in good agreement with the initial slope of \( M_s \) vs Li content \( x \).

The decrease in \( M_s \) with \( x \) may alternatively be a result of a decrease in Curie temperature with lithiation. To exclude this possibility, the Curie temperature of three lithiated samples was compared with that of the pristine powder. As seen in Fig. 10, the Curie temperature decreases only by about 10°C upon inserting 0.2 mol Li per formula unit, which cannot account for the large changes in room-temperature \( M_s \).

As the Li content increases, \( d^2-d^2 \) and \( d^3-d^3 \) interactions become more dominant, both of which are antiparallel. This suggests that the structure will have little or no net magnetization as it approaches \( x = 1 \). A loss in moment may also arise from the gradual disruption of the crystalline rutile structure at high \( x \), evident from the XRD data.

Finally, the irreversibility of the magnetic and structural properties, compared with the electrochemical cyclability, is attributed to structural changes or amorphization during the discharge/charge cycles.

**Conclusion**

This study shows that it is possible to create large changes in the magnetization of \( \text{CrO}_2 \) via electrochemical lithiation at room temperature or at 60°C. In the low-Li regime, below about \( x = 0.2 \) in \( \text{Li}_x\text{CrO}_2 \), a large change in magnetization of \( 20 \pm 2 \% \) per 0.1 Li/formula unit is obtained, and is in reasonable agreement with a model (which predicts a 25% change) for the reduction of \( \text{Cr}^{4+} \) to \( \text{Cr}^{3+} \) to balance charge as \( \text{Li}^+ \) is inserted. The change in magnetization is partly reversible, especially at low Li contents (for \( x = 0.1 \)). Electrochemically and structurally, the changes appear to be reversible for \( x \approx 0.1 \), and the partial reversibility of the magnetic changes may indicate the presence of defects such as vacancies in the structure after the discharge–charge cycling, to which the magnetic moment is very sensitive. The kinetics and reversibility of the process are improved at 60°C, and Li contents up to \( x = 0.9 \) could be inserted into the structure. At these concentrations the room-temperature moment is reduced to \(<5\%\) of its initial value. This decrease is irreversible due to disruption of the rutile crystal structure of the \( \text{CrO}_2 \).

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