Lithium Insertion in LiCr3O8, NaCr3O8, and KCr3O8 at Room Temperature and at 125°C

Koksbang, R.; Fauteux, D.; Norby, P.; Nielsen, K. A.

Published in:
Journal of The Electrochemical Society

Link to article, DOI:
10.1149/1.2096695

Publication date:
1989

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Lithium Insertion in LiCr$_3$O$_8$, NaCr$_3$O$_8$, and KCr$_3$O$_8$ at Room Temperature and at 125°C

R. Koksbang* and D. Fauteux*†

H&L Engineering, Vestergade 24, 5700 Svendborg, Denmark

P. Norby

Institute of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

K. A. Nielsen

Institute of Mineralindustry, Technical University of Denmark, 2800 Lyngby, Denmark

ABSTRACT

Lithium insertion and deinsertion reactions have been carried out with LiCr$_3$O$_8$, NaCr$_3$O$_8$, and KCr$_3$O$_8$ chemically and electrochemically at room temperature and at 125°C. The electrochemical experiments were performed with a nonaqueous liquid electrolyte at room temperature and with a polymer electrolyte at high temperature. At both temperatures, LiCr$_3$O$_8$ inserts chemically and electrochemically ca. 4 and 5 Li per formula unit, respectively. Experimental data reveal that the reaction involves major structural changes. Insertion of only small amounts of Li leads to irreversible structural breakdown. At elevated temperatures, the isostructural compounds NaCr$_3$O$_8$ and KCr$_3$O$_8$ are able to accommodate more than 4 Li/MCr$_3$O$_8$. During this process, minor structural changes are observed. At room temperature, NaCr$_3$O$_8$ and KCr$_3$O$_8$ also accommodate Li topotactically, but the maximum number of Li inserted per formula is close to 4 Li/NaCr$_3$O$_8$ and 1.3 Li/KCr$_3$O$_8$. Lithium ion diffusion coefficients are similar for the two compounds in the comparable composition range. Thermally, the fully lithiated compounds appear to be as stable as the pristine materials.

In chromium-oxygen compounds, prepared by conventional high-temperature/pressure methods, chromium tends to be present as Cr(III), Cr(VI), or as a mixture of these two oxidation states. Attempts to prepare ternary chromium oxides containing other transition metals and chromium in intermediate oxidation states usually fails due to a self-redox reaction in which chromium is stabilized as Cr(III) and/or Cr(VI) while the transition metal is either oxidized or reduced, respectively. Similarly, attempts to prepare mixed-oxidation-state chromium oxides usually leads to dismutation, e.g.,

$$3\text{Cr(IV)} \rightarrow 2\text{Cr(III)} + \text{Cr(VI)}$$

or

$$3\text{Cr(V)} \rightarrow \text{Cr(III)} + 2\text{Cr(VI)}$$

However, apart from Cr$_2$O$_3$, tetravalent chromium occurs in, e.g., CrO$_3$, A$_2$CrO$_4$, and A$_3$CrO$_5$ compounds (A = group IIA metal) (1), while pentavalent chromium occurs in hypochromates, e.g., Ba$_3$CrO$_4$, Li$_2$CrO$_4$, and K$_2$CrO$_4$ (2,3). Insertion/deinsertion reactions of alkali metal ions in transition metal oxides often lead to unusual products impossible to prepare by conventional methods and are thus a possible route to chromium oxides containing chromium in intermediate or mixed oxidation states.

Lithium and sodium extraction has been investigated in the layered oxides LiCr$_3$O$_8$ and NaCr$_3$O$_8$ by both chemical and electrochemical methods (4). Partial change of the oxidation state from +3 to +4 is observed in both systems without structural changes. In materials research for lithium battery systems, various binary chromium oxides have been investigated (5-10). The main interest has focused on Cr$_2$O$_3$ and Cr$_3$O$_4$ due to the high specific energies observed for the Li/CrO$_x$ couples, exceeding 1000 Wh/kg for Li/Cr$_3$O$_4$. These oxides apparently contain only Cr(III) and Cr(VI) (11), and lithium insertion presumably only involves reduction of Cr(VI) to lower oxidation states (5). Although the structures of Cr$_2$O$_3$ and Cr$_3$O$_4$ are still unknown, and the lithiated products are X-ray amorphous, it was suggested that the lithium insertion reaction is topotactic (5).

Contrary to Cr$_2$O$_3$ and Cr$_3$O$_4$, the structures of the three ternary chromium oxides LiCr$_3$O$_8$, NaCr$_3$O$_8$, and KCr$_3$O$_8$ are known. The structure of LiCr$_3$O$_8$ is shown in Fig. 1a and that of the two isostructural compounds NaCr$_3$O$_8$ and KCr$_3$O$_8$ are shown in Fig. 1b. The LiCr$_3$O$_8$ structure is composed of (Li, Cr)$_2$O$_4$ octahedra, which forms staggered strings by edge sharing in the direction of the c-axis, and CrO$_4$ tetrahedra which connects the octahedra strings to a three-dimensional framework by corner sharing. Each tetrahedron is in contact with three different strings. The lithium and chromium atoms are randomly distributed on the octahedral sites (12). Similarly, the (Na, K)-type is made of CrO$_4$ octahedra and CrO$_4$ tetrahedra that form layers by corner sharing. The layers are held together by the interlayer alkali metal atoms. The oxygen coordination number of sodium and potassium is 10 (13).

The close similarity of the two structures is obvious if the layers of the (Na, K)-type are packed closer together. In this way the coordination number of the Na or K is reduced to 6 as in LiCr$_3$O$_8$. The metal-oxygen arrangement is now the same in both structures when the random distribution of lithium and chromium in LiCr$_3$O$_8$ is not taken into consideration (14). The observed octahedral and tetrahedral chromium-oxygen distances differ considerably and are in agreement with the chromium-oxygen distances expected from

---

* Electrochemical Society Active Member.
† Present address: Mead Imaging, Miamisburg, Ohio 45342.

Fig. 1. LiCr$_3$O$_8$ (a) and (Na, K)Cr$_3$O$_8$ (b) structures shown as oxygen tetrahedra/octahedra representation projected on the (011) and (101) plane, respectively (12).
standard ionic radii for Cr(III) and Cr(VI), respectively (15). Measurements of the magnetic susceptibility (16) and x-ray photoelectron spectrum (17) of KCr$_3$O$_8$ support the crystallographic conclusion that chromium is essentially present as trivalent chromium (octahedra) and hexavalent chromium (tetrahedra) in the ratio 1:2.

The structure adopted by NaCr$_3$O$_8$ and KCr$_3$O$_8$ provides possible lithium diffusion paths in two dimensions between the (Cr$_7$O$_{18}$) layers. Within the layers and parallel to them are one-dimensional channels of ca. 1 Å diameter, which are larger than the average interlayer spacing. In LiCr$_3$O$_8$, these channels are the only diffusion paths left in the structure. Eight four-coordinated sites per unit cell corresponding to four lithium atoms inserted per formula unit can be identified inside the channels.

The observed oxygen coordination around chromium is tetrahedral for Cr(VI) and Cr(V), tetrahedral or octahedral for Cr(IV), and octahedral for Cr(III) (2). It should therefore be possible to reduce the tetrahedral Cr(VI) to Cr(IV) without major structural rearrangements, corresponding to four lithium per formula unit. Reduction of Cr(VI) to Cr(III) must lead to structural breakdown.

Except for a preliminary paper on lithium and sodium insertion in these oxides at elevated temperature (15), they seem to have been neglected so far. At temperatures above 100°C, all three compounds are able to accommodate more than four lithium atoms per formula unit corresponding to 85%–110% of full oxidation state.

In the present paper, the previous work has been extended to room temperature lithium insertion/deinsertion reactions, and a comparison is made with the results obtained at elevated temperature.

**Experimental**

The chromium oxides were prepared by heating 2:1 molar ratio mixtures of CrO$_3$ (Merck, p.a.) and M$_2$Cr$_2$O$_7$ (Merck, p.a.) placed in quartz crucibles to 350°C in open air for ca. 2h (18). Deviation from stoichiometry was induced by variation of the preparation conditions. In the following the compounds will be referred to as MCr$_3$O$_8$ irrespective of the actual compositions reported in Table I. Excess Mn$_2$Cr$_2$O$_7$ could be removed by washing with distilled water because the black MnCr$_3$O$_8$ compounds are insoluble in water (18).

X-ray diffraction diagrams of NaCr$_3$O$_8$ and KCr$_3$O$_8$ were in good agreement with the literature (13-14) and no other phases were observed. LiCr$_3$O$_8$ proved to be more difficult to obtain in the pure state. Additional lines caused by binary chromium oxides formed by decomposition of LiCr$_3$O$_8$ were recorded on a Perkin Elmer 883 spectrophotometer using either the potassium bromide tablet technique or nujol mulls. No differences were observed between the two types of spectra.

Polymer electrolyte films of 25-50 μm thickness were solvent cast on an insert substrate from an acetonitrile solution of PEO (M.W. 6-10$^6$, BDH) and LiCF$_3$SO$_3$ (Flourad FC 124, 3M) in the molar ratio 9:1 and dried overnight at 60°C in vacuum. Composite cathodes were solvent cast from acetonitrile solutions/suspensions on Ni foil and dried at 120°C under vacuum. The composition of the cathodes was 50-60% weight percent MCr$_3$O$_8$, 10% acetylene black, and 30-40% w/o PEO/LiCF$_3$SO$_3$, and the thickness was ca. 50 μm. Cells were assembled by placing a cathode on one side of a piece of polymer electrolyte (50 μm thick) and a cleaned piece of lithium foil on the other side. The cells were mounted between spring-loaded Ni-plated brass disks and housed in sealed brass containers.

The liquid electrolyte used was 0.5M LiCF$_3$SO$_3$ in propylene carbonate, vacuum distilled over sodium, and further dried with freshly cut lithium pieces. The cathodes were made by mixing 50 w/o MCr$_3$O$_8$, 10 w/o acetylene black, and 40 w/o binder and pressing 1 cm$^2$ cathode pellets under a pressure of 3 tons/cm$^2$. Two-electrode cells were assembled by separating a cleaned lithium foil anode and a cathode pellet with a Celgard 2400 porous polypropylene O-ring sealings.

Three-electrode cells were made as described elsewhere (23) using LiAl reference electrodes and Ni-foil current collectors. An Al strip was wrapped in Celgard 2400 separator soaked with electrolyte, and the anode and cathode were placed on each side of the batch. The cells were assembled between glass plates and inserted into a glass container filled with ca. 50 ml electrolyte and closed with a metal lid fitted with an O-ring seal. The α-Al/β-LiAl reference electrode was formed by shorting the lithium counter-electrode and the Al electrode until a stable voltage of about 300 mV vs. lithium, corresponding to α-Al/β-LiAl phase equilibrium, was reached.

Lithium was inserted and deinserted by passing a constant current through the cells. The degree of insertion was calculated from the amount of charge passed through the cells. Lithiated samples for x-ray diffraction analysis were prepared by applying a preset, constant voltage to cells kept at 125°C, until the current was stabilized below 1 μA.

### Table I. Composition and lattice parameters of Li$_x$M$_{1-x}$Cr$_3$O$_8$. Uncertainty ca. 5% on composition. The standard deviations on lattice parameters are given in brackets.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Vol. (Å$^3$)</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCr$_3$O$_8$</td>
<td>8.402(1)</td>
<td>5.478(2)</td>
<td>6.799(2)</td>
<td>91.44(10)</td>
<td>316.2</td>
<td>n-BuLi</td>
</tr>
<tr>
<td>Na$_{0.5}$Cr$_3$O$_8$</td>
<td>8.567(1)</td>
<td>5.464(1)</td>
<td>6.804(1)</td>
<td>91.43(1)</td>
<td>316.4</td>
<td>LiI, n-BuLi</td>
</tr>
<tr>
<td>Li$<em>{0.25}$Na$</em>{0.75}$Cr$_3$O$_8$</td>
<td>8.403(1)</td>
<td>5.475(1)</td>
<td>6.801(1)</td>
<td>91.42(2)</td>
<td>316.2</td>
<td>n-BuLi, Br$_2$</td>
</tr>
<tr>
<td>Li$<em>{0.5}$Na$</em>{0.5}$Cr$_3$O$_8$</td>
<td>8.494(1)</td>
<td>5.476(1)</td>
<td>6.804(1)</td>
<td>91.43(1)</td>
<td>316.4</td>
<td>n-BuLi, I$_2$</td>
</tr>
<tr>
<td>Li$_2$Na$_2$Cr$_3$O$_8$</td>
<td>8.495(2)</td>
<td>5.474(1)</td>
<td>6.803(1)</td>
<td>91.42(2)</td>
<td>316.3</td>
<td>n-BuLi, Br$_2$</td>
</tr>
<tr>
<td>Li$_3$Na$_3$Cr$_3$O$_8$</td>
<td>8.496(2)</td>
<td>5.475(1)</td>
<td>6.803(1)</td>
<td>91.44(1)</td>
<td>316.4</td>
<td>n-BuLi, I$_2$</td>
</tr>
<tr>
<td>KCr$_3$O$_8$</td>
<td>8.569(1)</td>
<td>5.466(1)</td>
<td>6.722(1)</td>
<td>95.29(10)</td>
<td>355.5</td>
<td>n-BuLi, I$_2$</td>
</tr>
<tr>
<td>K$_{0.25}$Cr$_3$O$_8$</td>
<td>8.567(1)</td>
<td>5.464(1)</td>
<td>6.821(1)</td>
<td>95.26(2)</td>
<td>355.3</td>
<td>n-BuLi, Br$_2$</td>
</tr>
<tr>
<td>Li$<em>{0.5}$K$</em>{0.5}$Cr$_3$O$_8$</td>
<td>8.570(2)</td>
<td>5.464(1)</td>
<td>6.762(1)</td>
<td>95.26(1)</td>
<td>355.4</td>
<td>n-BuLi, Br$_2$</td>
</tr>
<tr>
<td>Li$_2$K$_2$Cr$_3$O$_8$</td>
<td>8.572(3)</td>
<td>5.462(1)</td>
<td>6.761(2)</td>
<td>95.23(3)</td>
<td>355.3</td>
<td>n-BuLi, Br$_2$</td>
</tr>
<tr>
<td>Li$_3$K$_3$Cr$_3$O$_8$</td>
<td>8.578(2)</td>
<td>5.461(1)</td>
<td>6.763(2)</td>
<td>95.21(2)</td>
<td>355.6</td>
<td>n-BuLi, Br$_2$</td>
</tr>
</tbody>
</table>
for at least 12h. The cathodes were dissolved in acetonitrile, and the remaining solids were filtered off, washed repeatedly with acetonitrile, and vacuum dried at ca. 60°C. To avoid possible reactions with the atmosphere, some of the samples were coated with kollodium (Merck). However, no difference was observed between x-ray diagrams of materials protected from moisture, etc., and samples exposed to the atmosphere for time periods up to several weeks.

Room-temperature OCV curves of the materials were obtained by passing a known amount of charge through the cells followed by current interruption. The cell potentials were measured after voltage equilibration.

Cyclic voltammetry and ac measurements were conducted on three-electrode cells using a Solartron 1250 frequency response analyzer and a Solartron 1256 electrochemical interface.

Handling of the cell components and cell assemblage, as well as the chemical reactions, took place in either an argon-filled glove box (Braun, <10 ppm H2O) or in a dry room with relative humidity less than 2%.

**Results and Discussion**

Electrochemical lithium insertion: LiCr3O8 constant-current voltage-composition curves obtained at 125°C and at room temperature are shown in Fig. 2a and 3a. At 125°C, three voltage plateaus are observed. At ca. 2.9V for 0 < x < 0.65, at ca. 2.25V for 0.65 < x < 2.5, and at ca. 1.8V for 3.5 < x < 5. Basically, the curves at both temperatures are identical with the exception that the room-temperature voltage (cutoff at 1.5V) is lower than the high-temperature data (cutoff at 1.5V). Continued lithium insertion below 1.5V at 125°C results in a sharp voltage drop to less than 1V vs. lithium. The same capacity, ca. 5 lithium per formula unit, is obtained at both temperatures. As seen in Fig. 2 and 3, it was only possible to deinsert lithium partly from Li1LiCr3O8 at both temperatures, and the second and following lithium insertion curves are different from the initial discharge curves. It was therefore expected that an irreversible structural change of the pristine material is involved in the discharge process. The hump observed at ca. x = 0.3 during the second discharge at room temperature is also observed at 125°C, but it is not as pronounced as at room temperature. The hump is likewise visible during the following discharges. A possible explanation is a rise of the electronic conductivity consistent with the mixed oxidation states of chromium necessarily present during the insertion and deinsertion processes.

The lithium insertion at 125°C in NaCr3O8 and KCr3O8 appears to proceed quite differently from that in LiCr3O8 (Fig. 2), despite the initial structural similarities. For both NaCr3O8 and KCr3O8 the lithium insertion takes place at a virtually constant voltage, around 2.75V for x < 2. For lithium insertion in the range 2 < x < 3, the voltage curve is sloping while a second plateau develops at x > 3. The maximum number of lithium atoms inserted per formula unit exceeds four. Here also, the second and following lithium insertion curves are different from the initial ones, indicating as for LiCr3O8, that irreversible phase transformation takes place.

X-ray diagrams of Li1LiCr3O8, 0 < x < 5 (potentiostatic lithium insertion at 125°C), confirm that the reaction involves structural breakdown of the pristine material. All the x-ray diagrams show identical diffraction patterns indicating that the structure breaks down upon insertion of small amounts of lithium. Similar analysis of KCr3O8 shows that the structure is retained during electrochemical insertion of at least 2.5 lithium atoms per formula unit at 125°C. Continued lithiation of Li1KCr3O8 (x > 4) apparently leads to more severe structural changes in accordance with the change in oxygen coordination around chromium by reduction of Cr(IV) to Cr(III). Due to the poor quality of the x-ray diagrams (line broadening), it was impossible to calculate and refine unit cell parameters of the preserved phases and a proper identification of the reaction products of the displacement reactions was not possible either (15).

At room temperature, the effects of the structural differences between NaCr3O8/KCr3O8 and LiCr3O8 are more pronounced than at 125°C (Fig. 3). Less than one lithium is accepted by KCr3O8 above 1V vs. lithium. After a sharp initial voltage drop, the voltage decreases gradually from ca.
2.75V to ca. 1.60V (x = 0.45) after which the voltage is fairly constant until ca. x = 0.65, where the voltage drops abruptly by 200-300 mV. The shape of the NaCr$_3$O$_8$ discharge curve seems to be a combination of the LiCr$_3$O$_8$ second discharge curve at high voltage and that of KCr$_3$O$_8$ at lower voltage. Abruptly charged by 200-300 mV. The shape of the NaCr$_3$O$_8$ discharge curve is sloping, even though the initial capacity of the former lies below that of NaCr$_3$O$_8$ and KCr$_3$O$_8$. However, the shapes of the second and following discharge curves of NaCr$_3$O$_8$ and KCr$_3$O$_8$ are similar, even though the initial capacity of the former lies between that of LiCr$_3$O$_8$ and KCr$_3$O$_8$.

The OCV curves of Li/NaCr$_3$O$_8$ and Li/KCr$_3$O$_8$ cells obtained by intermittent constant-current lithium insertion and deinsertion at room temperature are shown in Fig. 4 and 5. The NaCr$_3$O$_8$ OCV curve has essentially the same shape as the corresponding constant-current curve. However, the number of Li atoms inserted is close to four. The OCV curve for KCr$_3$O$_8$ is sloping and nearly featureless for x < 1, while two small plateaus are seen at ca. 1.65 and 1.2V. Approximately 1.5 Li atoms are inserted per formula unit.

As pointed out by Besenhard et al. (7), lithium ion diffusion coefficients determined on polycrystalline materials in porous cathodes should be understood as apparent values rather than material constants because of the uncertainties involved in the determination of, e.g., effective surface area, particle size, and orientation effects. It therefore appears to be of interest to investigate the compositional dependence of the apparent diffusion coefficient. Lithium diffusion coefficients were determined by the galvanostatic intermittent titration technique described by Wepner and Huggins (24) using the equation

$$D_{Li} = 4\pi \cdot (V_m \cdot I_s \cdot F \cdot z)^2 \cdot \frac{(dE/dx)(dE/d(t^{1/2}))}{(dE/dx)}$$

where $D_{Li}$ is the lithium diffusion coefficient (cm$^2$/s), $V_m$ the molar volume (cm$^3$/mole), $I_s$ the current (A), $S$ the contact area of the sample-electrolyte interface (cm$^2$), $z$ is the valence of Li$^+$, $F$ is the Faraday constant, $dE/dx$ is the slope of the OCV curve, and $dE/d(t^{1/2})$ is the slope of the square root $t$ curve. The area was taken as the geometrical area of the porous cathodes used. Lithium diffusion coefficients were determined for lithium insertion in both NaCr$_3$O$_8$ and KCr$_3$O$_8$ (Fig. 4 and 5) as a function of the degree of insertion. During lithium insertion in NaCr$_3$O$_8$, $D_{Li}$ decreases linearly by several orders of magnitude in the insertion range 0 < x < 1.3. For x > 3, $D_{Li}$ increases abruptly to near the initial value. Similar trends are observed for lithium insertion in KCr$_3$O$_8$, although the degree of insertion does not exceed 1.3 Li/KCr$_3$O$_8$. Also, the diffusion coefficients have similar values in the insertion range 0 < x < 1.3 (10$^{-8}$-10$^{-13}$ cm$^2$/s). Thus, the lower degree of lithium insertion in KCr$_3$O$_8$ compared to NaCr$_3$O$_8$ is not caused by a slower lithium diffusion process. This is surprising in view of the structural and chemical similarities between these two compounds, but is possibly explained by either the larger channel diameters of KCr$_3$O$_8$ causing a pinning of the lithium ions at the channel walls thereby blocking the channels for further lithium insertion, or by the larger size of the potassium ion, 1.55Å, as compared to 1.24Å for the sodium ion (25). Due to the larger size, potassium might block the diffusion paths for lithium ion movement.

The reversibility of the reactions is limited by the ability to remove the inserted lithium ions as seen by repeated lithium insertion at both 125°C and room temperature. The capacity leveled off at x < 1 in Li$_x$M$_{1-x}$Cr$_3$O$_8$ for all the compounds at room temperature, and also Li$_x$Cr$_3$O$_8$ at 125°C. In NaCr$_3$O$_8$, more than three lithium atoms per formula unit could be repeatedly inserted above 3.7V at 125°C (15), although the polymer electrolyte used is electrochemically unstable above 3.5V at this temperature (26).

The average oxidation state of +5 of chromium in MCr$_3$O$_8$ allows the possibility of deinsertion of the alkali metal ion and simultaneous oxidation of the chromium to a higher average oxidation state. As mentioned in the introduction, it is possible to oxidize Cr(III) to Cr(IV) without introducing major structural changes, as is demonstrated in LiCr$_2$O$_3$ and NaCrO$_2$. The deinsertion of alkali metal ions from MCr$_3$O$_8$ was investigated by cyclic voltammetry in oxidation of freshly prepared cells. At a scan rate of 0.5 mV/s, no appreciable cathodic current was observed up to 4V vs. lithium. It therefore appears that the alkali metal ions in the pristine materials are immobile.

AC spectroscopy.—The behavior of the three chromium oxide composite cathodes was characterized upon electrochemical lithium insertion by ac spectroscopy at room temperature. The results obtained for these three cathodes were coherently analyzed according to the model proposed by Thomas et al. (27) which involves the formation of a surface layer at the cathode-electrolyte interface, through which ions have to migrate before charge transfer can occur.

All three chromium oxide cathodes show similar ac spectra composed of two series-connected convoluted RC equivalent components. In Fig. 6, complex plane impedance spectra obtained with LiCr$_3$O$_8$ as a function of voltage are presented. The first RC component, at higher frequency, was in this case invariant between 3.0 and 1.2V. It is believed that this RC component is related to the surface layer ($R_s$, 25 Ω/cm$^2$, $C_s$, 0.6 μF/cm$^2$). The second component of the spectrum had a larger resistance at 3V ($R_2$, 500 Ω/cm$^2$), which decreased markedly upon insertion of small amounts of lithium, down to $R_2$ = 65 Ω/cm$^2$, then remaining constant until x = 4.5 (Fig. 7a). For
insertion levels higher than \( x = 4.5 \), the value of \( R_s \) goes through a minimum followed by an increase. These latter variations of \( R_s \) occur in the insertion range where Cr(IV) is reduced to Cr(III). The variation of the capacitive terms and of the relaxation times as a function of the insertion level are shown in Fig. 7b. They indicate, as does the variation of the resistive terms, that changes occur mainly after insertion of small amounts of lithium \( (x < 1) \) and when Cr(IV) is reduced to Cr(III).

In the case of NaCr\(_3\)O\(_8\), a similar general behavior was observed even if smaller amounts of lithium could be inserted. In Fig. 8, we report the variations of the RC parameters of the ac spectra, as a function of the insertion level. For this system components the \( R_s \) and \( C_d \) vary for \( x < 1 \), then remain almost constant for \( 1 < x < 4 \). Since \( \tau_d \) was constant for all values of \( x \), the observed variations of \( R_s \) and \( C_d \) could be attributed to geometrical variations of the active cathode. However, x-ray results indicated no phase change and only minor volume changes of the unit cell (see later). Also, values of \( R_s \), \( C_d \), and \( \tau_d \) are all greater than those calculated for the LiCr\(_3\)O\(_8\) cathode. This result indicates that the nature of the surface layer is different in the two systems.

The values of \( R_s \) after an initial increase for \( x < 0.5 \), decrease continuously until \( x = 4 \), which could also indicate an increase of the active surface area. This is not confirmed by the variation of \( C_d \), which remains almost constant at ca. 800-1000 \( \mu F/cm^2 \) over the active range of \( x \). This value of \( C_d \) is much larger than the one calculated for LiCr\(_3\)O\(_8\).

The results obtained with KCr\(_3\)O\(_8\) are closely related to those for NaCr\(_3\)O\(_8\). Thus, the LiCr\(_3\)O\(_8\), NaCr\(_3\)O\(_8\)-, and KCr\(_3\)O\(_8\)-based cathodes all showed the formation of a surface layer for which the composition and rate-determining step is different for the LiCr\(_3\)O\(_8\) compared to the Na and K chromium oxides. The active surface areas for charge transfer are larger for the (Na, K)Cr\(_3\)O\(_8\) (based on \( C_d \)) than for LiCr\(_3\)O\(_8\), even if structural breakdown was observed only for LiCr\(_3\)O\(_8\). These results indicate that the mechanism by which lithium is electrochemically inserted in the chromium oxides can differ markedly, and that the achieved level of insertion depends more on the intragranular diffusion coefficient than on \( R_s \).

**Chemical lithium insertion.**—All three compounds retain their black color, independent of the extent of insertion. The composition and refined lattice parameters for NaCr\(_3\)O\(_8\), KCr\(_3\)O\(_8\), and the corresponding lithiated compounds are given in Table I. The composition of the lithium form of MCr\(_3\)O\(_8\) was Li\(_2\)Cr\(_3\)O\(_8\). Contrary to the behavior of NaCr\(_3\)O\(_8\) and KCr\(_3\)O\(_8\), lithiation of LiCr\(_3\)O\(_8\) leads to structural breakdown.

**Reaction with LiI.**—LiI is a mild lithiation reagent. The reaction corresponds to ca. 2.8 V vs. lithium (22), which again by comparison with the discharge curves (Fig. 3-5) corresponds to less than 0.5 Li/MCr\(_3\)O\(_8\) inserted electrochemically. As is seen in Table I, the number of lithium atoms inserted chemically in NaCr\(_3\)O\(_8\) and KCr\(_3\)O\(_8\) per formula unit is ca. 0.5. In LiCr\(_3\)O\(_8\), 0.6 lithium atom was inserted per formula unit.

**Reaction with n-BuLi.**—Reaction with n-BuLi corresponds to 1.0 V vs. lithium (22). By reacting LiCr\(_3\)O\(_8\), NaCr\(_3\)O\(_8\), and KCr\(_3\)O\(_8\) with n-BuLi, the same trend is observed as during electrochemical lithium insertion; ca. four lithium atoms per formula unit are inserted in LiCr\(_3\)O\(_8\) and less than one in KCr\(_3\)O\(_8\). The amount of lithium accepted by NaCr\(_3\)O\(_8\) lies between that of LiCr\(_3\)O\(_8\) and KCr\(_3\)O\(_8\).

**Delithiation with I\(_2\).**—Contrary to n-BuLi, the I\(_2\) system is reversible (22). Thus, lithium extraction with I\(_2\) of the highly lithiated compounds Li\(_2\)MCr\(_3\)O\(_8\), should result in the same stoichiometry as lithiation of the pristine materials with LiI, provided the reaction is reversible. The data

---

**Fig. 6.** Room-temperature complex plane ac impedance spectra of Li\(_{1-x}\)Cr\(_3\)O\(_8\)-based composite cathode at the following potentials, (a) 2.1 V, (b) 1.9 V, (c) 1.6 V, and (d) 1.3 V in the frequency range 65–0.1 Hz and an amplitude of 25 mV. The units of Z and Z' are ohm.

**Fig. 7.** (a, left) Variation of \( R_s \) and (b, right) variation of (●) \( \log(C_d) \), (□) \( \log(\tau_d) \), (+) \( \log(C_a) \), and (∗) \( \log(\tau_a) \) as functions of insertion level (∗) in Li\(_{1-x}\)Cr\(_3\)O\(_8\) at room temperature.
in Table I show that this is indeed the case for the Li/KCr₃O₈ system, the same number of Li/KCr₃O₈ are present in the two compounds. For both LiCr₃O₈ and NaCr₃O₈ more than twice the amount of lithium is present in the compounds (3.7 Li/LiCr₃O₈ and 1.2 Li/NaCr₃O₈) after treatment with n-BuLi and I₂ than after treatment with LiI.

Delithiation with Br₂.—Chemical delithiation with Br₂ corresponds to electrochemical charging to ca. 3.5V (22) vs. lithium, and bromine is therefore capable of deinserting more lithium than iodine. Furthermore, the bromine potential vs. lithium is higher than the OCVs of the pristine materials (3.1-3.2V vs. Li). It is expected that bromine deinserts at least the amounts of lithium inserted, but it also deinserts part of the alkaline metals present in the pristine materials, provided they are mobile. However, lithium is still present in all three compounds after deinsertion with bromine (Table I and 0.9 Li/LiCr₃O₈) and decreasing in the order LiCr₃O₈ > NaCr₃O₈ > KCr₃O₈. The potassium content is practically unchanged in all the experiments while the sodium content is decreasing, probably due to ion exchange with lithium.

X-ray diffraction experiments reveal that the structures of NaCr₃O₈ and KCr₃O₈ are preserved during both lithiation and delithiation. The x-ray diagrams were indexed in the same space group as the pristine materials (C2/m) and unit cell parameters were refined using program CELLKANT (31). Contrary to the expectation that lithium insertion leads to an increased layer distance (expansion parallel to the c-axis), the data indicate a small increase of the a-axis, i.e., within and parallel to the (Cr₃O₈)ₙ layers (Table I). The variations of the b and c unit cell axes are insignificant, as are the volume changes of the unit cells.

IR spectroscopy.—For LiCr₃O₈ both electrochemical data and x-ray analysis show that the structure breaks down during lithium insertion. However, for NaCr₃O₈ and KCr₃O₈ the electrochemical data indicate irreversible structural changes upon cycling, while x-ray analysis shows that the structures of the pristine materials are preserved. Further characterization of the lithium insertion in these two compounds was therefore necessary.

The Cr(VI)—O bonds are considerably shorter than the Cr(III)—O bonds, and therefore have higher stretching frequencies. The main absorption bands of Cr(VI)—O bonds are present between 700 and 800 cm⁻¹ (28, 29), Cr(V)–O stretching frequencies are reported to appear at ca. 815 cm⁻¹, as in, e.g., Li₃CrO₄ (30). Therefore, a gradual lowering of the chromium-oxygen vibrational stretching frequencies is expected when Cr(VI) is progressively reduced to chromium in lower oxidation states by lithium insertion. Accordingly, the variations of the stretching frequencies were followed by IR spectroscopy.

NaCr₃O₈ and KCr₃O₈ contain one Cr—O bond which is considerably shorter than all the other Cr—O bonds. For KCr₃O₈, this bond length is 1.53Å as compared to 1.65Å for the remaining tetrahedral Cr—O bonds and ca. 1.95Å for the octahedral Cr—O bonds. The oxygens of the latter groups are shared between octahedra and tetrahedra and give rise to the absorption bands at ca. 800 cm⁻¹ as well as the overall complexities of the spectra. The short Cr—O bond is correlated to one CrO₄ tetrahedra only and can be considered to be a Cr—O double bond associated with the absorption bands at ca. 900 cm⁻¹ (28).

The IR spectra, in the region 300-1200 cm⁻¹, of NaCr₃O₈ and KCr₃O₈ as well as of the chemically lithiated and delithiated compounds, are shown in Fig. 9. At frequencies above 1200 cm⁻¹, all spectra are essentially featureless. The spectra of LiCr₃O₈ (not shown) and KCr₃O₈ agree well with the spectra reported by Foster and Hambly (20).

Insertion of 0.9 Li/MCr₃O₈ in KCr₃O₈ causes a shift of the high-frequency absorption at 902-894 cm⁻¹. Furthermore, an absorption shoulder appears at ca. 700 cm⁻¹. The variation in bonding character induced by treatment with LiI,
as well as lithium deinsertion with Li and Br, are too small to be detected in this case.

The stretching frequency of the Cr=O double bond of NaCrO$_3$ decreases from 886 to 880 cm$^{-1}$ by reaction with n-BuLi. The overall features of the spectrum of the original material are still visible, although a broad absorption band appears in the range 750-500 cm$^{-1}$. A similar treatment of Li$_2$CrO$_3$ (not shown) results in a broad absorption band with a maximum at ca. 500 cm$^{-1}$ consistent with almost complete reduction of Cr(VI) to Cr(III). Delithiation of NaCrO$_3$ and KCrO$_3$ leads to an increase of the stretching frequencies to the values observed for the pristine materials.

Apparently, chromium is present in mixed oxidation states between Cr(VI) and Cr(III) in both NaCrO$_3$ and KCrO$_3$ during lithium insertion, and the oxygen coordination around chromium is essentially preserved.

Thermal stability.—The DSC traces of NaCrO$_3$ and KCrO$_3$ and the corresponding n-BuLi-treated compounds are shown in Fig. 10. The compounds were examined in the temperature range 300-600°C. As no reactions were observed at lower temperatures, only the range 300-600°C is shown.

The most remarkable feature is that the lithiated compounds appear to be as thermally stable as the pristine materials. For both KCrO$_3$ and NaCrO$_3$, only one endothermic reaction is observed, at 453° and 456°, respectively. The thermal behavior of the lithiated compounds deviates both from each other and from those of the pristine materials. By heating of Li$_x$NaCrO$_3$, an exothermic reaction at 389°C precedes an endothermic reaction at 419°C. Heating of Li$_x$KCrO$_3$ shows an exothermic reaction at 391°C, followed by two endothermic reactions at 393° and 422°C, respectively. In addition, a broad exotherm is observed at 501°C.

X-ray analysis of samples heated to 600°C revealed the presence of Cr$_2$O$_3$ as the major constituent of the decomposition products of both Li$_3$NaCrO$_3$ and Li$_3$KCrO$_3$. No dichromates were observed, consistent with the decomposition of the lithium, sodium, and potassium dichromates at temperatures below 600°C. Contrary to Li$_2$Cr$_2$O$_7$ and Na$_2$Cr$_2$O$_7$, which decompose at around 400°C, K$_2$Cr$_2$O$_7$ decomposes at 500°C and the DSC peak observed at 501°C for Li$_2$KCr$_2$O$_7$ may thus be associated with this reaction. A proper identification of the compounds besides Cr$_2$O$_3$ from the x-ray diagrams was not possible. These compounds are probably chromates of the types (Li, Na)$_2$CrO$_4$ and (Li, K)$_2$CrO$_4$.

**Fig. 10.** Comparison of DSC traces of Li$_x$MCr$_2$O$_7$ (M = Na, K) and the pristine materials. The materials were contained in closed Pt ampuls and the heating rate was 10°C/min. The peak temperatures are indicated in the figure.

**Conclusion**

At temperatures above 100°C, all three materials are able to accommodate more than four lithium atoms per formula unit. At room temperature, however, both chemical and electrochemical evidence shows that the amount of lithium inserted decreases with increasing size of the alkali metal ion present in the pristine materials. The experimental data also show different lithium insertion reactions.

As at elevated temperatures, LiCrO$_3$ takes up ca. five lithium atoms per formula unit at room temperature, but the pristine material is prone to irreversible structural breakdown during lithium insertion at both temperatures, and the reactions seem to be identical. The structural breakdown already takes place upon insertion of small amounts of lithium, and the reaction is irreversible. Lithium insertion in NaCrO$_3$ and KCrO$_3$ at both temperatures proceeds quite differently from that in LiCrO$_3$. At a current density of 0.1 mA/cm$^2$, less than two and one Li/LiCr$_2$O$_7$ are inserted, respectively, at room temperature. Complete reduction of all Cr(VI) to Cr(III) demands six Li/LiCr$_2$O$_7$. However, the insertion of more than four Li/LiCr$_2$O$_7$ involves reduction of Cr(IV) to Cr(III), and a change of oxygen coordination around chromium is therefore to be expected.

A detailed structural knowledge regarding the sites occupied by lithium in the lithiated NaCrO$_3$ and KCrO$_3$ is lacking. Although the shape of the discharge voltage indicates structural changes, x-ray, IR, and DSC analyses of chemically lithiated compounds show that the structure is preserved during lithium insertion.

By galvanostatic intermittent current lithium insertion at room temperature, close to four lithium atoms are inserted in NaCrO$_3$ while only ca. 1.3 lithium is inserted in KCrO$_3$. This difference is surprising since the two compounds are isostructural and x-ray analysis of chemically lithiated compounds shows that the structure is preserved during lithium insertion.

**Acknowledgment**

The authors wish to thank S. Ye Andersen, H&L Engineering, J. Engell, and The Technical University of Denmark for helpful discussions.

Manuscript submitted June 20, 1988; revised manuscript received Aug. 18, 1988.

H&L Engineering assisted in meeting the publication costs of this article.

**REFERENCES**

Degradation Mechanisms of Nylon Separator Materials for a Nickel-Cadmium Cell in KOH Electrolytes


Hughes Research Laboratories, Malibu, California 90265

ABSTRACT

Degradation reactions of a nylon 6 battery separator material have been studied in 4-34% aqueous KOH electrolytes at 35°-110°C. In a Ni/Cd cell, this degradation involves a slow hydrolysis reaction followed by fast electrochemical oxidations of the hydrolysis reaction products. Arrhenius activation energy of the hydrolysis reaction in 34% KOH was 20.0 ± 0.3 kcal/mole. A plot of the hydrolysis rate at 100°C vs. hydroxyl ion concentration gave a rate maximum at about 16% KOH, and the mechanism for this effect is discussed. Electrochemical oxidations of the hydrolysis product, 6-aminocaproate ion, appear to proceed rapidly in several sequential steps at a nickel oxide electrode. In a Ni/Cd cell, the combination of nylon separator hydrolysis followed by electrochemical oxidation of the products can seriously degrade the battery lifetime. The rate of the hydrolysis of nylon 66 separator material was approximately one half of that of the nylon 6 material.

A nonwoven nylon felt (Pellon 2505) which is made of nylon 6 has been used as a standard separator material in aerospace Ni/Cd battery cells. Until recently, this battery has been used almost exclusively as the energy storage device for long life spacecraft such as communication satellites. The lifetime of these batteries was previously one of the life limiting factors of the spacecraft, particularly due to the degradation of the nylon separator material as we had reported earlier (1). Although the problem of nylon degradation was recognized previously (2), there has been relatively little quantitative work published on the mechanism and rate of the degradation. Our preliminary study showed that the chemical and electrochemical degradation of nylon can cause lifetime problems for the Ni/Cd cell. Therefore, it is important for the battery industry to understand the degradation rate and mechanism of the nylon materials in Ni/Cd cells. Although for high-power satellites (approximately 2 kW or higher) the battery is being replaced by newly developed Ni/H_2 batteries, the Ni/Cd battery is expected to remain as the workhorse for smaller power satellites. Ni/Cd cells with alternate nylon material (Pellon 2536) are recently being developed as the Pellon 2505 became unavailable commercially. In other cell designs, nylon separators are replaced with a zirconia separator (3-7).

*Nylon is known to degrade in neutral media by air oxidation (9). However, limited information was available on the base hydrolysis of nylon 6 of which the separator material is made. A close monomeric structure to this nylon may be e-caprolactam which has an analogous peptide bonding to the nylon. The e-caprolactam was reported (10) to follow the first-order kinetics of a chemical reaction with respect to its concentration and first-order in hydroxyl ion concentration.

The present report describes results of our accelerated studies on the nylon felt hydrolysis as a function of temperature and KOH concentration and the electrochemical oxidations of the nylon hydrolysis product at a nickel oxide electrode, and also includes a discussion of a possible mechanism of the hydrolysis. The hydrolysis rates of a nylon 66 felt material are compared with those of nylon-6 felt. Activation energy of the hydrolysis rates has been determined. Nylon degradation rates at an operation temperature of a Ni/Cd cell can be estimated using this activation energy and elevated temperature data.

Experimental

Reagents.—Potassium hydroxide used in the study was Baker analyzed reagent grade. Acetonitrile (AN) was “distilled in glass” grade by Burdick and Jackson Laboratories, Incorporated. Bis-(trimethylsilyl)acetamide (BSA) was a specially purified grade by Pierce Chemical Company. Bis-2-(2-methoxyethoxy)ethyl ether (BME) purchased from Aldrich Chemical Company. Reagent-