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Chromium Oxides and Lithiated Chromium Oxides. Promising Cathode Materials for Secondary Lithium Batteries

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Chromium oxides and lithiated chromium oxides were synthesized by thermal decomposition of chromium trioxide (CrO₃) at high temperatures and oxygen pressures. Synthesis temperature and pressure markedly affect the performance of these cathode materials. Higher pressures lead to a higher O/Cr ratio and fewer impurities in the final product. These materials are stable intercalation hosts for lithium, and exhibit a higher capacity than any of the prominent positive electrodes used in secondary lithium batteries. m-CrO₃ has a capacity of 255 mAh/g, while m-LiCrO₂ has a capacity of 210 mAh/g, during the first discharge. The average voltage of these cells is 3.0 V vs. Li/Li⁺ that gives an average energy density of approximately 650 Wh/kg.

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Rechargeable lithium batteries based on chromium oxides as the active cathode material are of considerable interest because of the very high theoretical specific energies of these compounds.¹ Varta developed a primary Li/CrO₃ cell which has a specific energy of 270 Wh/kg and with an energy density of 675 Wh/L at low drain rates.² Toyoguchi et al.³ developed a coin-type LiCr₂O₄ secondary battery with an energy density of 170 Wh/L and a cycle life of over 400 cycles. According to Yamamoto and co-workers,⁴,⁵ the best performance of the chromium oxide cathode was obtained with amorphous Cr₂O₃ cathodes due to the higher surface roughness of the amorphous cathode. Primary Li/AgCr₂O₄ cells, utilizing organic electrolytes, are manufactured by SAFT.⁶ Bessenhard et al.⁷ studied chromium oxides as cathodes for secondary high energy density lithium batteries. According to these studies Cr₂O₃ and Cr₂O₅ have an average discharge voltage of approximately 3.0 V vs. Li/Li⁺ and a maximum charge transfer equivalent one electron per Cr atom.

The objectives of this work are to synthesize chromium oxides (CrO₃), lithiated chromium oxides (m-LiCrO₂ and LiCr₂O₄), and to characterize these materials as positive electrodes for secondary lithium batteries.

Experimental

Crystalline CrO₃ was obtained by heating CrO₃ (Aldrich, 99.9%) in an autoclave for 24 h at high temperatures under high oxygen pressure. The autoclave was connected with a pressure gauge and temperature controller to monitor and control the pressure and temperature. The synthesis temperatures and pressures used in the preparation of various chromium oxides are reported in Table I. Sample A was prepared at 320°C, while all other samples were prepared at 270°C. The synthesis pressure used was ca. 50 psi for samples A and B, and 400 and 500 psi for samples C and D, respectively. The product was a mixture of CrO₃ and residual Cr₂O₃. The reaction was stopped by quenching the steel cylinder in cold water followed by cooling in a stream of cold air.

Chemically modified CrO₃ (m-CrO₃) was prepared by thermal decomposition of Cr₂O₃ in the presence of 2% [(NH₄)₂SO₄ (Aldrich, 99.999%) at 270°C and 500 psi. The Cr₂O₃ impurity was removed by leaching the product five times in distilled water for 1 h. The chemical treatment (as described above) helps in increasing the dispersive state and active surface area of m-LiCrO₂.

Electrochemical characterization of the cathode materials was carried out in Swagelok three-electrode cells (T-cell). The anode and reference electrodes were disks of lithium foil, and the separator was a sheet of Whatman glass fiber filter paper. The cathode consisted of a mixture of 87% CrO₃ (or m-LiCrO₂), 8.7% carbon black, and 4.3% poly(tetrafluoroethylene) which was pressed into a thin film 50-60 μm thick.

The electrolyte used in this study was 1 M LiPF₆ in a 1:1:3 mixture of propylene carbonate, ethylene carbonate, and dimethyl carbonate (EM Industries). The procedure for the fabrication of electrodes and cells are almost the same as those described previously in detail.⁸ Handling of materials and cell assembling was carried out in an Ar-filled glove box (Vacuum Atmospheres, < 5 ppm H₂O).

The X-ray diffraction (XRD) patterns were collected with a Rigaku 4055S X-ray diffractometer using Cu Kα radiation. The surface area of these oxides was measured using Micrometrics 270 BET (N₂ adsorption).

Cyclic voltammograms for m-CrO₃, m-LiCrO₂, and LiCr₂O₄ were obtained using a scan rate of 0.05 mV/s over a potential range of 2.0-4.3 V vs. Li/Li⁺. The cell performance was evaluated galvanostatically at current density of 0.1 and 0.5 mA/cm² at room temperature. The cells were cycled (charge-discharge) on Bitrode (Bitrode Co, MO, USA) cycler within the cutoff potentials.

Results and Discussion

The stoichiometry of the CrO₃ samples was determined by a Perkin Elmer TGA7 thermal gravimetric analyzer. The O/Cr ratio was determined by reducing the CrO₃ samples to Cr₂O₃ in air at 1°C/min. The decomposition of CrO₃ to Cr₂O₃ starts at 385°C. The knowledge of final product stoichiometry (Cr₂O₃) and weight loss (corresponding to O₂ lost or evolved) lead to O/Cr ratio as reported in Fig. 1a. A sample thermal gravimetric analysis (TGA) curve (sample C) and atomic ratios of O/Cr for other chromium compounds are also shown in the figure. The purity of chromium oxides was found to depend on the synthesis pressure and temperature. By increasing the oxygen pres-

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Table I. Synthesis conditions for different chromium oxides prepared in this study.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Temperature (°C)</th>
<th>Pressure (psi)</th>
<th>Chemical treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>320</td>
<td>50</td>
<td>No</td>
</tr>
<tr>
<td>B</td>
<td>270</td>
<td>50</td>
<td>No</td>
</tr>
<tr>
<td>C</td>
<td>270</td>
<td>400</td>
<td>No</td>
</tr>
<tr>
<td>D</td>
<td>270</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td>m-CrO₃</td>
<td>270</td>
<td>500</td>
<td>Yes</td>
</tr>
</tbody>
</table>

sure more pure product was obtained (see sample D and m-CrO$_x$). As shown in Fig. 1a, the electrode with the highest O/Cr ratio (2.653) has a stoichiometry close to Cr$_3$O$_8$. The diffractograms of m-CrO$_x$ and m-LiCrO$_x$ are shown in Fig. 1b. The crystallinity of the m-CrO$_x$ oxide host lattice suffers severely during chemical lithiation.

The particle size of both lithiated and nonlithiated chromium oxide is in the range of 2-4 μm. The particle size of lithiated CrO$_x$ appears to be slightly smaller than that of CrO$_x$. Brunauer-Emmett-Teller (BET) surface area determinations (N$_2$ adsorption) show surface areas of 2 and 3.45 m$^2$/g for CrO$_x$ and m-LiCrO$_x$, respectively. The morphology of chromium oxide particles is not clear but it may be described as an aggregation of small particles. Apparently, the size and shape of the particles have not changed considerably by lithiation.

Figure 2 shows the first discharge curves for various chromium oxides prepared at different temperatures and pressures. Sample D and chemically modified chromium oxide m-CrO$_x$ were prepared at higher pressures compared to samples B and C. The initial capacity of m-CrO$_x$ is 255 mAh/g. The oxides prepared at lower pressures have impurities, which result in a small plateau at the start of discharge. As shown in Fig. 2, the plateau decreases as the pressure increases, and disappears completely in the case of m-CrO$_x$. Also, the average voltage depends on the synthesis temperature and pressure of the active material. The voltage increases from 2.5 to 3.0 V as the pressure in the autoclave is increased. The reversibility of m-CrO$_x$ cathode material was tested using cyclic voltammetry. Figure 3 shows a cyclic voltammogram for CrO$_x$ obtained at 0.05 mV/s. The voltage was varied between 2.0 and 4.3 V. As shown in Fig. 3, this cathode material is very reversible over the entire intercalation range with a small capacity loss after the first discharge. The structural change during intercalation was avoided by not allowing Cr(VI) to reduce to Cr(III), which may result in structural breakdown.

Figure 4 shows the capacity of m-CrO$_x$ as a function of cycle number. The capacity after 50 cycles is still 210 mAh/g. The initial capacities of commercial cathode materials (LiMn$_2$O$_4$, LiCoO$_2$, and LiNiO$_2$) are also shown for comparison in the same graph. Cycling of samples B, C, and D was stopped after the first few cycles because their capacity was lower than the capacity of m-CrO$_x$. All electrodes were cycled at the discharge rate of 0.1 mA/cm$^2$. High capacity and small capacity fade make m-CrO$_x$ an attractive cathode material in secondary lithium batteries.

Figures 5a and b show cyclic voltammograms of LiCr$_2$O$_4$ and m-LiCrO$_x$, respectively, obtained at a sweep rate of 0.05 mV/s. The voltage was varied between 1.0 and 4.0 V for LiCr$_2$O$_4$ and between 2.0 and 4.3 V vs. Li/Li$^+$ for m-LiCrO$_x$. As shown in Fig. 5a, two peaks are observed at 1.6 and 3.25 V during intercalation, and two peaks at 2.1 and 3.8 V during deintercalation. The separation between the peaks indicated high irreversibility with a large capacity loss between
the first and second cycle. Figure 5b shows that only one peak was obtained during intercalation (at 3.5 V) in m-LiCrO$_x$ and one peak during deintercalation at 3.2 V vs. Li/Li$.^+$. The small peak separation indicates that this cathode material is reversible over the entire intercalation range.

Figures 6a and b show the charge-discharge curves obtained for LiCr$_3$O$_8$ and m-LiCrO$_x$. The electrode in Fig. 6a was cycled between 1.0 and 4.0 V vs. Li/Li$.^+$ reference electrode. As shown in this figure, the Li$_2$Cr$_2$O$_7$ structure is not stable and after the first cycle two plateaus appear with a large capacity loss. Similar results were observed by Koksbang et al.$^{12}$ They found that the Li insertion/deinsertion reaction in Li$_2$Cr$_2$O$_7$ involves irreversible structural changes with the presence of three plateaus at ca 2.9, 2.25, and 1.8 V.

The charge-discharge curves for m-LiCrO$_x$ shown in Fig. 6b when cycled between 2.0 and 4.2 V at the rate of 0.1 mA/cm$^2$ showed an initial capacity of 210 mAh/g. Only one plateau was observed during charge and discharge indicating that the structure is stable and reversible over the entire intercalation range. The results clearly indicate that m-LiCrO$_x$ has different electrochemical characteristics than LiCr$_3$O$_8$ reported in literature. m-LiCrO$_x$ can be used as a positive electrode with any carbon negative electrode in a lithium-ion cell, while CrO$_2$ can be used with lithium or lithiated carbon as a negative electrode in lithium or lithium-ion secondary cells.

Conclusions

Chemically modified m-CrO$_x$ was synthesized by heating CrO$_3$ in an autoclave under high oxygen pressure. The CrO$_3$ impurity was removed by leaching and by chemically treating the product, thus making CrO$_x$ environmentally friendly. This compound is neither hygroscopic nor soluble in water. Synthesis temperature and pressure markedly affected the performance of CrO$_x$. Higher pressures resulted in higher O/Cr ratio and less impurities in the final product. The shape of the discharge curves and cyclic voltammograms indicate no structural changes during lithium insertion. The discharge capacity of m-CrO$_x$ exceeded 250 mAh/g, when cycled between 2.0 and 4.2 V, and the energy density of this electrode is ca. 600-650 Wh/kg. The electrode prepared from m-CrO$_x$ exhibited negligible capacity fade when cycled between 2.0 and 4.2 V at a current density of 0.1 mA/cm$^2$. This material can be used as a positive electrode with lithium or lithiated carbon as a negative electrode in secondary lithium cells.

The chemical lithiation of CrO$_2$ was carried out using active LiI in acetonitrile. Charge and discharge studies indicated that this material is stable and reversible over the entire intercalation range with an initial capacity of 210 mAh/g. m-CrLiO$_x$ can be used as a positive electrode with a carbon negative electrode in the lithium-ion cell.

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References