

Cathode Materials for Rechargeable Lithium-Ion Batteries

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New technologies, such as portable electronic devices and electric vehicles, drive the need for new and better battery technology.¹ Although the electrochemical systems used in modern batteries have not changed for decades, these batteries are not adequate for today's portable power needs.² A good battery must provide a stable, high potential during discharge, and must provide a high current per unit weight.³ Good reversibility is also necessary if the battery is to be rechargeable. Lithium batteries were first developed in the 1970's because lithium is the lightest of the highly reducing alkali metals, giving it the ability to provide a high potential while providing a lightweight source of current.⁴ Unfortunately, lithium metal is so reactive that it is hazardous when used in rechargeable batteries.⁵

"Lithium-ion batteries," originally called "lithium rocking-chair batteries," provide the solution to this safety issue (see Figure 1 below.)⁶

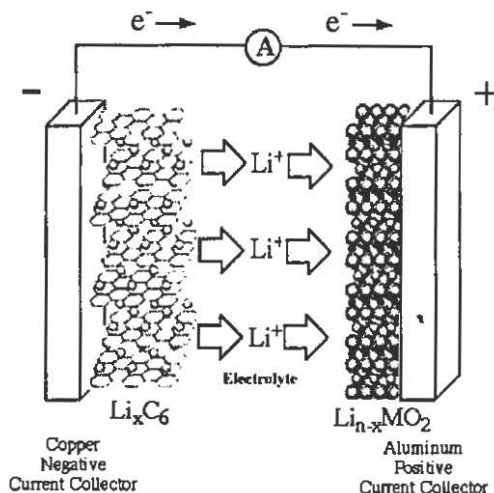
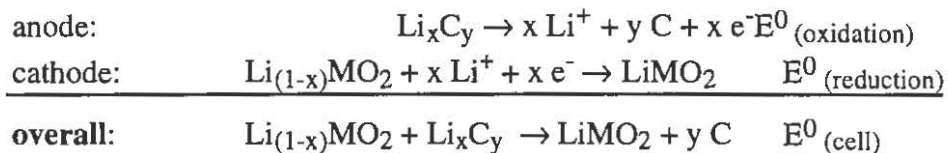


Figure 1. Schematic Diagram of a Lithium-Ion Cell⁷

Instead of metallic lithium, lithium-intercalated graphitic carbon provides the source of lithium ions at the anode.⁸ Lithium-intercalating transition metal oxides are used as cathode materials.⁹ The half-reactions and overall cell reaction are as follows:



Since graphitic carbon is widely used as an anode material, research is centered around developing new cathode materials for lithium-ion batteries.⁹

Three transition-metal oxides are suitable cathode materials for lithium-ion batteries: LiCoO_2 , LiNiO_2 and LiMn_2O_4 .¹⁰ The properties of these materials are compared in Table 1.

Table 1. Comparison of Cathode Materials In Use or Under Development¹¹⁻¹³

Type	Voltage (V vs. Li)	Capacity (mAh/g)	Cost (\$/kg)	Hazard	Cyclable Range (x in mol)	Li ⁺ Diffusivity (cm ² /s)
$\text{Li}_{(1-x)}\text{CoO}_2$	4.5	140	25	Toxic	$0.00 < x < 0.50$	10^{-8}
$\text{Li}_{(1-x)}\text{NiO}_2$	3.8	150	13	Carcinogen	$0.00 < x < 0.90$	10^{-8}
$\text{Li}_{(1-x)}\text{Mn}_2\text{O}_4$	4.0	120	0.5	None	$0.05 < x < 0.95$	10^{-9}

LiCoO_2 is currently used in several commercially-available lithium-ion batteries, including those used in Sony camcorders and IBM laptop computers. It has the highest voltage of the three candidates, resulting from the oxidation power of the $\text{Co}^{4+/3+}$ couple. The main disadvantages of using this material arise from its limited cycling lithium content range, its cost and its toxicity. The limited cycling range results from instability in the cathode as lithium ions are removed from the closest-packed oxygen lattice.¹⁴ The contraction of lithium-deficient layers and expansion of lithium-rich layers causes mechanical strain that cracks the cathode and breaks the conductivity in the cell. LiNiO_2 is a cheaper material than LiCoO_2 , and also has a higher cyclable capacity.¹² It is not currently used, however, because its capacity fades during cycling. This results from irreversible changes in its layered structure.¹⁵ It is also a carcinogen. LiMn_2O_4 is the cheapest and safest of these three materials, and so is the most desirable from a profitability standpoint. It also has the largest cyclable range of lithium content, resulting from its three-dimensional spinel structure.¹³ The spinel structure of LiMn_2O_4 also explains its lower lithium-ion diffusivity, as the three-dimensional pathways through the spinel do not provide as direct a diffusion path as the layered cobalt and nickel oxide structure. Unfortunately, the manganese oxide cathode has the lowest capacity, and suffers from capacity fading during cycling.¹⁶ As the battery is discharged, increased lithium content in the cathode ($x < 0.05$) causes a Jahn-Teller distortion of the manganese ions.¹⁶ This results in irreversible structure changes that adversely affect the ability of the cathode to deintercalate lithium. In addition, Mn(II) ions dissolve into the electrolyte through disproportionation of Mn(III) to Mn(II) and Mn(IV). The Mn(II) ions migrate to the anode and are reduced to metallic manganese, which leads to increasing cell resistance and polarization.¹⁷

Much of the current research on lithium-ion battery cathodes is centered around improving LiMn_2O_4 , since it is commercially the most attractive material. There are several approaches being taken to prevent its capacity loss during cycling. The first is to simply develop a new preparative technique which generates a more stable structure of the manganese oxide.¹⁸⁻²² Researchers have explored manganese oxide structures ranging from the spinel type to a layered compound analogous to the cobalt and nickel cathode materials, to amorphous sol-gel derived materials. A second approach is to include an excess of lithium in the cathode material, to promote structural stability during cycling. This approach is rewarding, except that cyclability is provided at the expense of capacity.¹⁸ Another approach to improving the

cyclability of the spinel-type manganese oxide cathode is to incorporate dopant metals to stabilize the Mn(III) oxidation state in the oxide.^{23,24} Promising results have been obtained, especially for chromium-doped manganese oxide (see Figure 2 below).²⁴

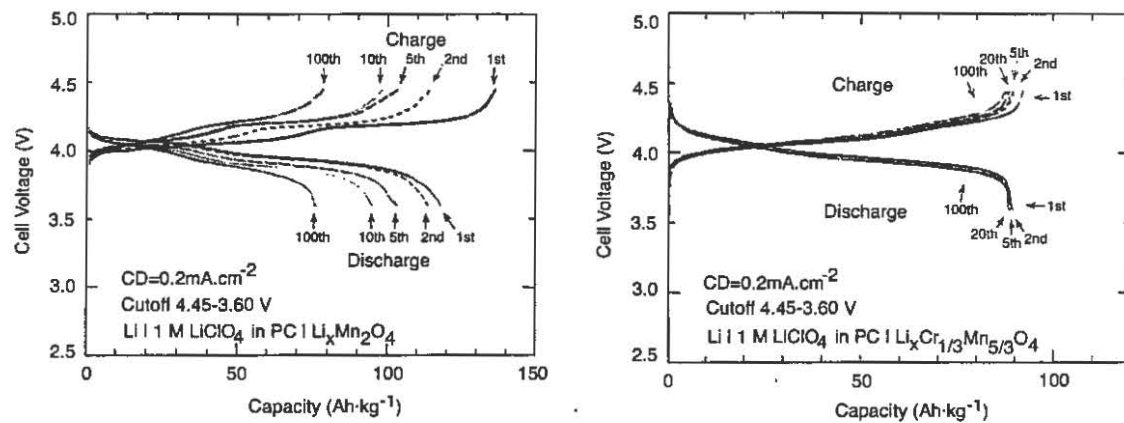


Figure 2. Cycling capacity-voltage plots for Li/Li_xMn₂O₄ and Li/Li_xCr_{1/3}Mn_{5/3}O₄ showing improved capacity retention of doped cathode²³

New materials have also been developed as cathodes for lithium-ion batteries. Ein-Eli and Howard reported the preparation of a mixed copper-manganese spinel material that acts as a 5 V cathode material.²⁵ Fey, et al., reported an inverse spinel LiNiVO₄ that has a potential of 4.8 V versus lithium metal.²⁶ Unfortunately, neither material is viable at this time, as there are no electrolytes available that are stable at the potentials necessary to use them.

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