

# Layered lithium cobalt oxide cathodes

Lithium cobalt oxide was the first commercially successful cathode for the lithium-ion battery mass market. Its success directly led to the development of various layered-oxide compositions that dominate today's automobile batteries.

The demonstration of a rechargeable lithium battery with a lithium metal anode and a layered  $\text{TiS}_2$  cathode in 1976 by Whittingham<sup>1</sup> prompted the investigation of a series of other transition metal dichalcogenides  $\text{MX}_2$  ( $M$  = transition metal and  $X$  = S or Se) as cathodes<sup>2</sup>. However, these investigations were soon met with two obstacles for practical cells. First, the use of a metallic lithium anode posed safety hazards due to dendrite growth from the anode that caused internal short circuiting. Second, the relatively small differences between the redox energies of dichalcogenides and lithium could only enable a moderate cell voltage (<2.5 V) with a lithium anode.

These impediments triggered Goodenough, at the University of Oxford, to explore alternative cathode materials. A fundamental understanding of the redox energies in solids by Goodenough<sup>3</sup> led him to consider layered oxide hosts in which the transition metal ion ( $M^{n+}$ ) could be in a high oxidation state. This is because a higher oxidation state of  $M^{n+}$  lowers its redox energy and consequently increases the cell voltage while also maintaining high electronic conductivity and structural stability. Accordingly, he focused on  $\text{Cr}^{3+/4+}$ ,  $\text{Fe}^{3+/4+}$ ,  $\text{Co}^{3+/4+}$  and  $\text{Ni}^{3+/4+}$  redox couples in layered  $\text{LiMO}_2$  oxides<sup>4</sup>. This led to the identification of a layered  $\text{LiCoO}_2$  as a cathode with a significant increase in cell voltage to 4 V compared to the dichalcogenide cathodes<sup>5</sup>.

Layered  $\text{LiCoO}_2$  exhibits several features necessary for a good cathode. The  $\text{Li}^+$  and  $\text{Co}^{3+}$  ions order well in alternate layers in  $\text{LiCoO}_2$  ensuring a good structural stability, the direct Co–Co interaction in the structure facilitates high electronic conductivity, and the interconnected lithium-ion sites support fast lithium-ion conductivity. These built-in favourable characteristics along with an easy synthesis of  $\text{LiCoO}_2$  in ambient air made it an appealing cathode.

Ironically, no battery company was interested in a patent on  $\text{LiMO}_2$  cathodes. At that time cells were assembled in a charged state (for example, the charged

$\text{PbO}_2$  cathode in the assembly of a lead–acid cell), whereas  $\text{LiCoO}_2$  is in a discharged state and the industry could not imagine assembling a cell with a discharged cathode even for a rechargeable cell. The University of Oxford was not interested in patenting the inventions of academic research. Therefore, Goodenough arranged for the Atomic Energy Research Establishment (AERE) Laboratory in Harwell, England, to file a patent, but the inventors signed away their rights.

Crucially, the discovery of the  $\text{LiCoO}_2$  cathode eliminated the necessity to use the hazardous metallic lithium anode because the cathode itself already possesses lithium. This allowed the use of a lithium-free host such as graphite as the anode, which in turn enabled the present-day lithium-ion battery concept in which the lithium ions shuttle between a lithium-free anode and an oxide cathode during the charge–discharge process<sup>6</sup>. This strategy also led the Sony Corporation to launch commercialization of the first rechargeable lithium-ion battery with a graphite anode and a  $\text{LiCoO}_2$  cathode.

Goodenough's group at Oxford also explored in the 1980s the analogous layered  $\text{LiNiO}_2$  as a cathode<sup>4</sup>. However, the practical viability of  $\text{LiNiO}_2$  is hampered by several challenges. The main difficulty is to synthesize it as a well-ordered material at high temperatures. At high temperatures,  $\text{Ni}^{3+}$  ions tend to be reduced to  $\text{Ni}^{2+}$  ions that occupy the lithium layer with a volatilization of lithium, resulting in a lithium-deficient  $\text{Li}_{1-y}\text{Ni}_{1+y}\text{O}_2$  phase<sup>7</sup>.

Since the 1980s, the field of layered oxide cathodes has evolved with the substitution of Mn to give  $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$  (NMC) and Al to give  $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$  (NCA). Early examples of such cathodes are  $\text{LiNi}_{0.333}\text{Mn}_{0.333}\text{Co}_{0.333}\text{O}_2$  (NMC 111) and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA 801505). Building on the success of these early compositions, the trend in the field has been to increase gradually the Ni content while reducing Mn and Co contents in NMC and to increase the Ni content and lower the Co content in NCA. The increasing Ni content allows the extraction of an increasing amount of

lithium during charge to give an increase in capacity without inducing undesired oxygen release from the lattice. Some examples are NMC 622, NMC 811 and NCA 920602. The presence of Mn in NMC makes the synthesis easier as Mn is present as  $\text{Mn}^{4+}$  and Ni is present as  $\text{Ni}^{2+}$ , which are both stable at the high synthesis temperatures.

Although  $\text{LiCoO}_2$  was the first material that enabled commercialization of the lithium-ion battery technology, the rapid increase in the electric vehicle market and the limited availability of cobalt are forcing the community to reduce cobalt or eliminate it altogether in layered oxide cathodes. The approaches have been to increase the Ni content with appropriate cationic substitutions in layered oxides (for example,  $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Al}_{0.05}\text{O}_2$  (NMA 900505)) in order to realize the necessary structural, chemical, cycle, thermal and air stabilities while also increasing the capacity<sup>8</sup>. Controlled synthesis and advanced characterization play a vital role in this endeavour. □

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