

Comments on the History of Lithium-Ion Batteries

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The first commercial lithium-ion (Li-Ion) battery appeared in 1991 (1). This announcement was preceded by several separate inventions that included the work of Goodenough (2), Yazami (3) and others. The use of the intercalated carbon/graphite anode eliminated the problems of poor lithium metal rechargeability due to the formation of dendrites and mossy lithium metal deposits with only a small (0.050 mV) voltage penalty. It also greatly increased the safety aspects of the high-energy battery system. A depiction of the operation of the Li-Ion cell is given in Figure 1. Both the anode and cathode are lithium intercalation compounds incorporated into polymer-bonded electrode structures based on polyvinylidene difluoride (PVdF). The polymer allows the structure to breath and accommodates the volume changes that occur in the active materials during charge and discharge. The cell operates by intercalation and de-intercalation of lithium ions into the anode and cathode depending on whether the cell is being charged or discharged. This has been referred to as a "swing," "rocking chair" or "lithium-ion" concept of cell operation. There is no lithium metal in the cell, only lithium ions. The electrolyte is a mixture of alkyl carbonate solvents with lithium hexafluorophosphate salt to provide conductivity.

The market for Li-Ion cells is driven by the demand of the portable electronic device market, especially the notebook computer and the cellular telephone. This market has had explosive growth. The growth in demand for higher performance battery systems is noted in Figure 2. Figure 3 shows the increase in capacity since the initial commercial introduction in for the cylindrical 18650 cells. This remarkable increase in capacity was realized through engineering improvements in the manufacturing processes and the introduction of new separator, cathode and anode materials. There has been a shift to a rectangular (prismatic) cell format in response to the needs of the principal applications. The development of new constructions based on polymer electrolytes have given designers the freedom of footprint and batteries with greater Wh/kg (4).

There has been an intense effort to develop new materials (5 - 8). The original lithium cobalt oxide has been modified by incorporating additives to stabilize the crystal structure and increase the capacity. New materials R&D has been very active in identifying new carbons to replace the original hard carbon anode. Graphites with a practical capacity up to 350 mAh/g have been identified. Other forms based on mesophase pitch precursor carbon fibers with surface treatments have capacities in excess of 350 mAh/g. Examples of alternate anode materials include lithium titanium oxide and nanostructured stabilized tin alloys. New cathode materials include lithium cobalt-nickel oxide, lithium manganese oxides, and lithium iron phosphates with an olivine structure. Emphasis in developing new materials has been related to improved safety along with higher capacity. Additives have been developed to lower the first cycle loss associated with the solid electrolyte interphase (SEI) layer that forms on the anode and cathode during cell operation. Other additives are designed to improve adhesion to the current collectors and to prolong cycle and storage life.

References:

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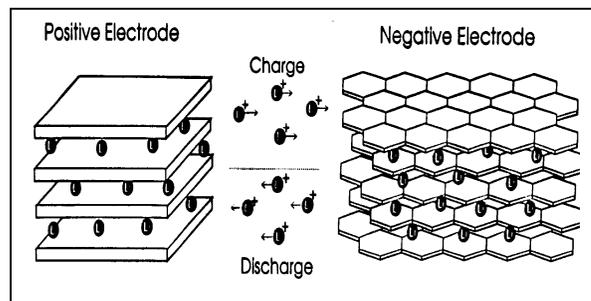


Figure 1. Depiction of the Charge-Discharge Operation of Li-Ion Cells.

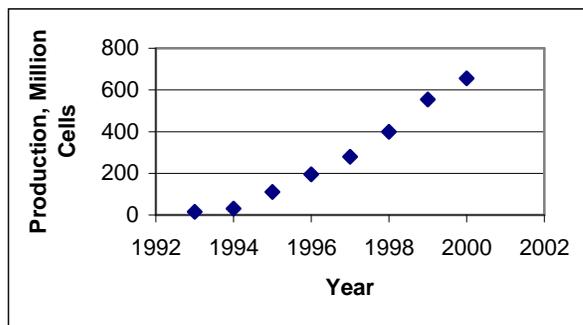


Figure 2. Growth in Market Demand of Li-Ion Cells

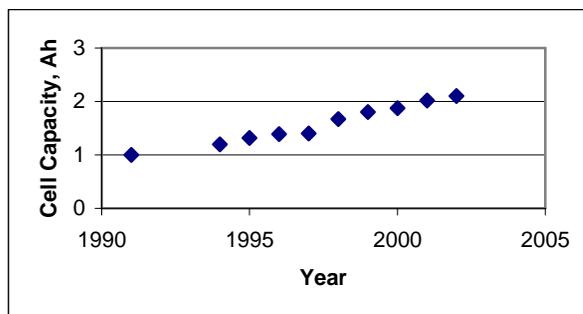


Figure 3. Increase in Capacity of ICR18650 Cells with Time