Basic principles of li-ion batteries

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Stanley Whittingham, John Goodenough and Akira Yoshino received the Nobel prize in chemistry in 2019 for development of the lithium ion battery. This technology was commercialized in the beginning of 1990s. The negative electrode is made of graphite and the positive electrode is composed of a layered oxide material, such as $LiCoO_2$. Electrolyte is lithium salt dissolved in an organic solvent. Active materials are typically formulated as nanoparticles and mixed with conductive additives and binders. The resulting ink is spread as thin layers on copper or aluminium foils acting as current collectors. The electrodes are wetted with the organic lithium conducting electrolyte, and separated by 10-20 μm thick porous plastic separator to prevent short circuits. The resulting cell is sealed airtight, while minimizing the amount of oxygen and moisture in the battery, illustrated in Figure 1.

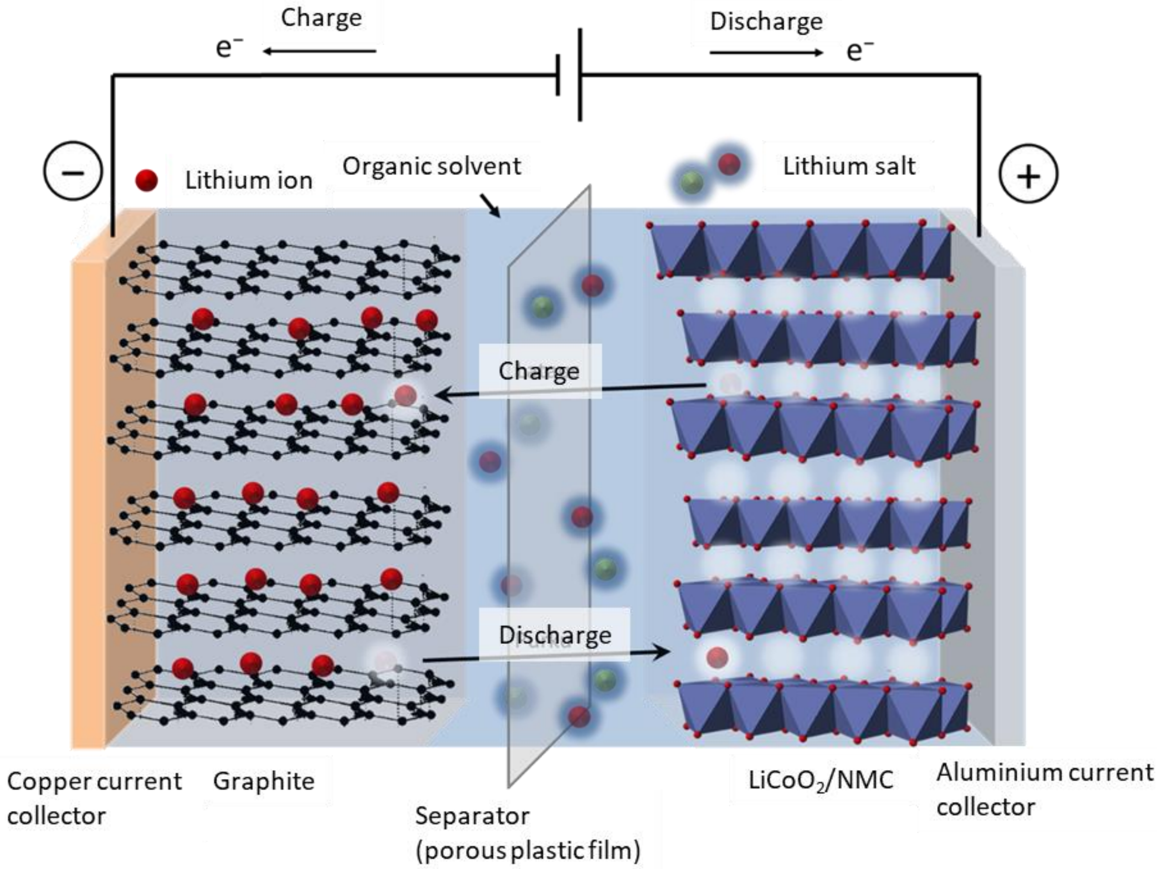

Figure 1. lithium ion battery, where lithium ions intercalated in the graphite are transported into layered oxide materials.

Single cells are assembled as battery packs by connecting the cells together in series or parallel. Serial connection allows increase of the pack voltage and parallel connection increases the output current. Battery charge density is defined by how many lithium ions can be intercalated into the crystal structure of the electrode materials. This can be calculated by Faraday's law of electrolysis if the reaction is known:

$Q = nFz$, where Q is the on varauksen määrä (in Coulombs, 1 C = 1 As), n is the molar amount (in moles, mol), F is the Faraday's constant 96 485 As/mol = 96 485 C/mol and z is the amount of electrons transferred in the reaction.

Intercalation reactions can be written in a general form as:

$Li^+ + S + e^- = Li^+\text{-}S$

Where S is a free site in the crystal lattice. The number of electrons is therefore 1 in the reaction. The negative electrode charge reaction is

$Li^+ + C_6 + e^- = LiC_6$

and happens at the potentials of 0.25 – 0.01 V vs. Li/Li^+ (referenced to the potential of the $Li^+ + e^- = Li$ reaction). One mole of graphite (C_6) can therefore theoretically intercalate one mole of lithium ions. One mole of graphite weights the molar weight of graphite, *M*, that is 6 x 12.01 g/mol = 72.06 g/mol. Gravimetric charge density of graphite is therefore

$Q / m = Fz/M$ = 96 485 As/mol x 1 / 72.06 g/mol = 1339 As / g. Typically Ah is utilized instead, (1 Ah = 3600 As = 3600 C), so the final value is given as 372 mAh / g. Volumetric charge density can be calculated if the density is known (2.29 g/cm^3), giving 850 mAh / cm^3.

On option for positive electrode material is cobalt oxide, CoO_2, resulting in discharge reaction

$Li^+ + Co(IV)O_2 + e^- = LiCo(III)O_2$

During discharge the oxidation state of the cobalt changes from +IV to +III, so cobalt is reduced in the reaction. Theoretical charge density can be calculated as for graphite, resulting in 274 mAh / g. The reaction happens at the potentials of ca. 3.7 V vs. Li/Li^+. Full discharge of the material would result in complete removal of the lithium ions form the lattice, destabilizing the structure. Therefore in practice the charge storage density is limited to ca. 165 mAh / g.

The full cell reaction is the sum of the different half cell reactions:

$$\begin{array}{rl} & Li^+ + C_6 + e^- = LiC_6 \\ + & \underline{LiCo(III)O_2 = Li^+ + Co(IV)O_2 + e^-} \\ & Li^+ + C_6 + e^- + LiCo(III)O_2 = LiC_6 + Li^+ + Co(IV)O_2 + e^- \end{array}$$

$$C_6 + LiCo(III)O_2 = LiC_6 + Co(IV)O_2$$

Cell voltage varies between 3-4.2 V depending on the state of charge, and is on average ca. 3.6 V.

The overall reaction must be in balance, so to allow utilization of the full capacity, both electrodes need to have the same charge capacity. Theoretical energy storage density can be calculated by multiplying the theoretical charge density by the average cell discharge voltage. The unit is V x mAh/g = mWh/g = Wh/kg. In practise als the weight of the other components like current collectors, electrolyte, separator and the housing sholud be considered. Typically the weight fraction of the active material can reach ca. 40% of the cell weight.