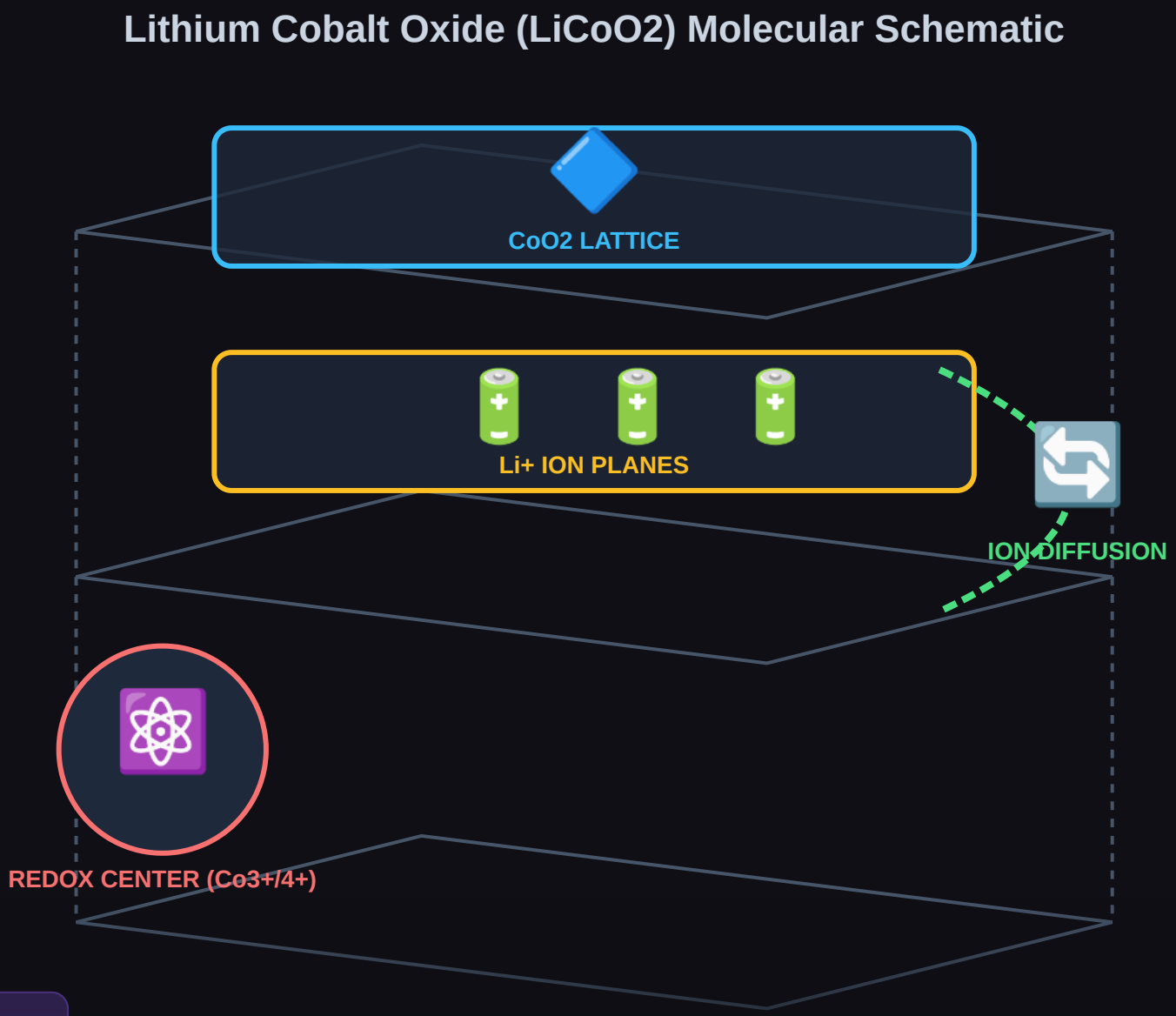

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Chemistry and crystal lattice structures of lithium cobalt oxide cathodes

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🔷 CoO2 Lattice Framework

The LiCoO2 cathode is built upon a skeletal framework of Cobalt ions surrounded by Oxygen atoms in an octahedral geometry. These CoO6 units share edges to form continuous two-dimensional sheets.

This layered rock-salt structure is highly stable under normal operating conditions. The oxygen layers provide the structural ‘floors’ and ‘ceilings’ between which lithium ions reside. The strength of the Co-O bond is critical for preventing the lattice from collapsing when lithium is extracted during the charging process.

🔋 Lithium Intercalation Planes

Lithium ions (Li+) occupy the octahedral sites between the CoO2 slabs. This ‘intercalation’ chemistry allows the ions to move in and out of the host structure without significantly altering the host’s fundamental identity.

In a fully discharged state, the layers are packed with Li+. As the battery charges, these ions are pulled out into the electrolyte. The spacing between the CoO2 layers (the c-axis) actually expands slightly when lithium is removed due to increased electrostatic repulsion between the oxygen layers that are no longer shielded by the positive Li+ ions.

⚛️ Redox Chemistry (Co3+/Co4+)

Energy storage in LiCoO2 is driven by the oxidation and reduction of Cobalt. When the battery charges, a Li+ ion leaves the lattice, and to maintain electrical neutrality, a Cobalt ion gives up an electron, transitioning from a Co3+ state to a Co4+ state.

This transition is the limit of the material’s capacity. If you attempt to remove more than about 50-60% of the lithium, the Co4+ becomes highly unstable and can start stripping electrons from the Oxygen atoms, leading to oxygen gas release and potentially thermal runaway.

🔄 Ion Transport Pathway

The layered nature of LiCoO2 facilitates ‘two-dimensional’ lithium diffusion. The ions move primarily within the planes between the CoO2 sheets rather than jumping through the sheets themselves.

The speed of this movement (diffusion coefficient) determines the power density of the battery—how fast it can charge and discharge. Factors such as grain boundaries, lattice strain, and the ‘order-disorder’ transition of lithium ions at specific concentrations can significantly impact how easily these ions navigate the crystal.