DESIGNING LITHIUM-ION BATTERY CATHODES

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LITHIUM-ION BATTERY
A DISCOVERY THAT CHANGED THE WORLD
EARLY WORK

1950-1980

• Magnetic materials for first RAM memory

• Cooperative atomic orbital ordering

• Rules for sign of magnetic interactions

• Solid sodium-ion electrolyte: NASICON
THE LITHIUM-ION BATTERY

HOW IT WORKS
WHAT FACTORS DETERMINE CHOICES FOR NEW BATTERY CHEMISTRY?

1. Cost
2. Energy
3. Power
4. Cycle Life
5. Safety
6. Environment
User Time = (Cell Voltage) x (Amount of Lithium ions Stored)
INSERTING LITHIUM

HOW THE CHEMISTRY WORKS

Titanium Sulfide
\( \text{TiS}_2 \)

Lithium Titanium Sulfide
\( \text{LiTiS}_2 \)
ENERGY DENSITY

FROM SULFIDE TO AN OXIDE

Density of States, N(E)

Li/Li⁺

Voltage limit in a sulfide, < 2.5 V

Increase in voltage to 4 V in an oxide

Co²⁺/³⁺: 3d

Co³⁺/⁴⁺: 3d

O²⁻: 2p

S²⁻: 3p
MATERIALS CLASS 1

1980: LAYERED OXIDE

Citation: Mizushima, Jones, Wiseman, Goodenough — Materials Research Bulletin 15, 783 (1980)

Lithium Cobalt Oxide
LiCoO\(_2\)

Lithium-deficient Cobalt Oxide
Li\(_{0.5}\)CoO\(_2\)
MATERIALS CLASS 2

1983: SPINEL OXIDE

Citation: Thackeray, David, Bruce, Goodenough — Materials Research Bulletin 18, 461 (1983)

Lithium Manganese Oxide
LiMn$_2$O$_4$

Manganese Oxide
Mn$_2$O$_4$
MATERIALS CLASS 3

1987-89: POLYANION OXIDE

Citation: Manthiram, Goodenough — Journal of Solid State Chemistry 71, 349 (1987)

Iron Sulfate
\( \text{Fe}_2(\text{SO}_4)_3 \)

Lithium Iron Sulfate
\( \text{Li}_2\text{Fe}_2(\text{SO}_4)_3 \)
MATERIALS CLASS 3

1997: POLYANION (OLIVINE) OXIDE

Citation: Padhi, Nanjundaswamy, Goodenough — Journal of the Electrochemical Society 144, 1188 (1997)

Lithium Iron Phosphate
LiFePO$_4$

Iron Phosphate
FePO$_4$
KEY FINDINGS

AND HISTORICAL SIGNIFICANCE

• A fundamental study of the properties of transition-metal oxides led to the identification of oxide cathodes

• Pushed boundaries at the intersection of solid-state chemistry and physics

• The three classes of materials discovered still remain the only viable cathodes — and the basis for future development

  - Layered oxide
  - Spinel oxide
  - Polyanion oxide
MOVING FORWARD

• Liberating society from fossil fuels
• Harvesting electric power from solar and wind energy
• Electricity storage as chemical energy is the key
• Affordable, safe battery technologies