Aalto University
School of Chemical
Engineering

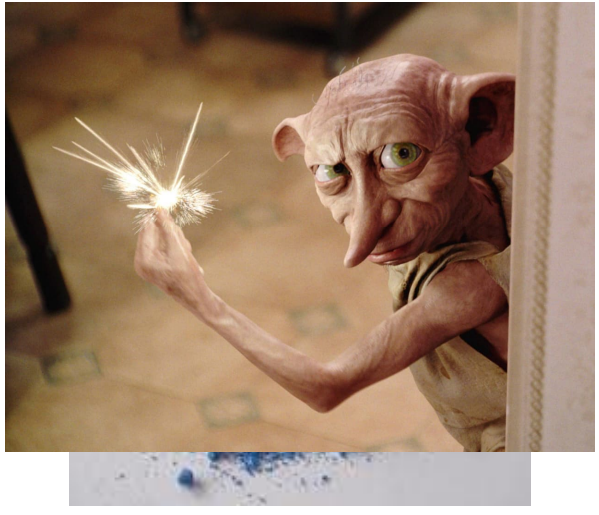
CHEM-E4130 - Chemistry of the Elements

Cobalt

6.10. 2023 Gabrielle Laurent & Yan Zheng

Discovery & Origin of name

Discovery date	1739 (1735)
Discovered by	Swedish chemist Georg Brandt
Origin of the name	The name is derived from the German word 'kobald', meaning goblin.
History	• Minerals containing cobalt were used by the early civilizations of Egypt and Mesopotamia for coloring and dyeing. • Cobalt blue was known even earlier in China (pottery glazes).



* The tomb of a Pharaoh, who ruled from 1361-1352 BC, contained a small glass object coloured deep blue with cobalt.

Cobalt - Element information, properties and uses | Periodic Table. Available at: https://www.rsc.org/periodic-table/element/27/cobalt (Accessed: 04 October 2023).

World production

- Cobalt is primarily extracted as a byproduct of copper and nickel mining.
- Over 70% of global cobalt supply comes from the Democratic Republic of Congo (DRC).
- Other significant countries include Russia, Australia, Canada, and the Philippines.

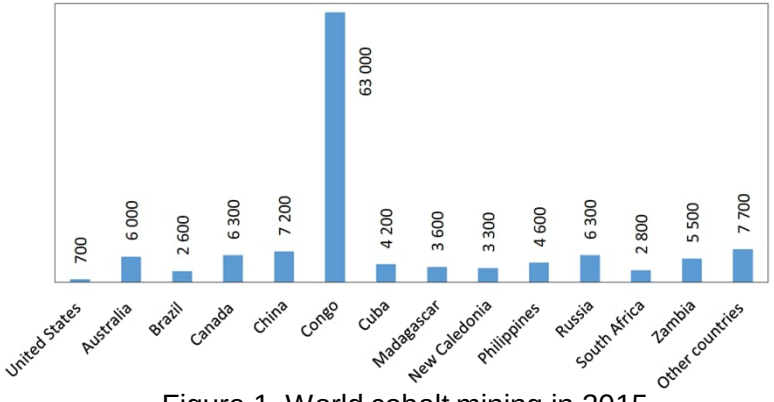


Figure 1. World cobalt mining in 2015.

- Cobalt prices have nearly tripled
- Due to increased demand driven by supply chain constraints
- Unpredictable scenarios for battery manufacturing

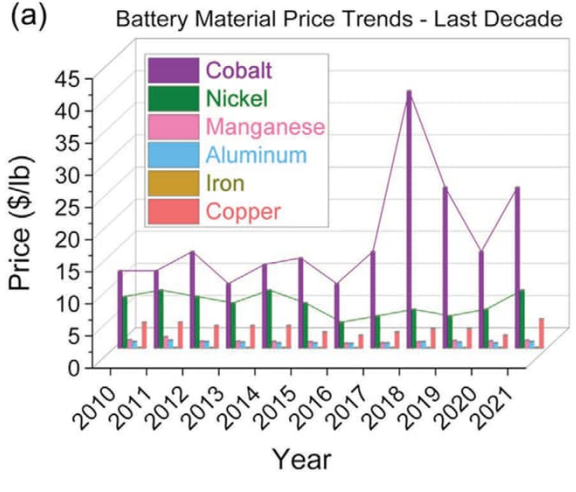
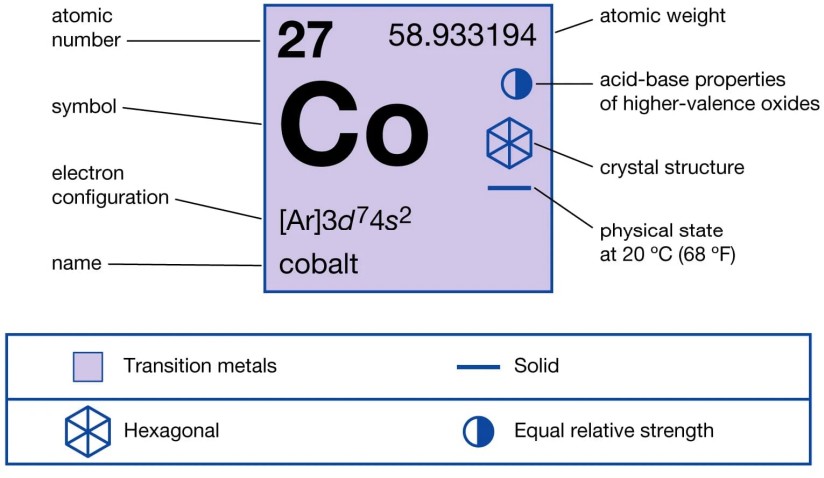


Figure 2. Battery material price trends from 2010 to 2021.

Pazik, P.M. *et al.* (2016) 'World production and possible recovery of cobalt from the Kupferschiefer Stratiform Copper Ore', *E3S Web of Conferences*, 8, p. 01063.
Muralidharan, N. *et al.* (2022) 'Next-Generation Cobalt-free cathodes – a prospective solution to the battery industry's cobalt problem', *Advanced Energy Materials*, 12(9).

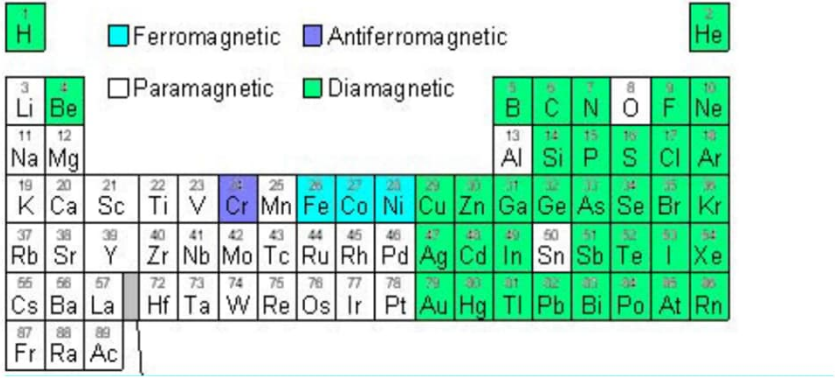
Characteristic



- **Melting point: 1492 degree**
- **Oxidation state:**
  - +2, +3, +4, +5
- **Atomic radius:**
  - 1,25 A
  - 0,75 A (+II)
  - 0,61 A (+III)

Britannica, https://www.britannica.com/science

Magnetism activity



- Its ferromagnetic properties is coming from is unpaired electron in 3d orbital
- Cobalt has a curie temperature of 1145 degree. Above 1145 degree, it will lose his ferromagnetic properties.

Mohapatra J. and all, Hard and semi-hard magnetic materials based on cobalt and cobalt alloys, Journal of Alloys and compounds, 824, 2020

Special features

1.Hardness: Cobalt is a hard metal with a Mohs hardness of 5.5, making it durable and resistant to wear and abrasion. It is commonly used in applications where hardness and strength are required, such as in cutting tools and high-strength alloys.

2.Corrosion resistance: Cobalt is relatively resistant to corrosion and oxidation, which makes it useful in environments where corrosion resistance is important, such as in marine and aerospace applications.

3.Unique color: Cobalt has a distinct blue color when it is in the form of a salt, which has led to its use in pigments and dyes, as well as in glass and ceramics to produce blue coloration.

4.Radioactive properties: Cobalt has some radioactive isotopes, such as cobalt-60, which are used in medical and industrial applications, including cancer treatment, radiography, and sterilization of food and medical equipment.

Geologyscience, https://geologyscience.com/ore-minerals/cobalt-ore/#Cobalt_Applications

Compounds

Cobalt alloys

Discovery:

- 1907 first patent on Cobalt Chromium Alloy by Elwood Haynes

Structure:

- Hexagonal close packed until 417 degree, after it will be face centered cubic
- Alloying compound like Cr/Md/Tg will increase the transformation temperature

Klarstrom D; and all, Cobalt Alloys: Alloying and Thermomechanical Processing, Encyclopedia of Materials: Science and technology, 1279-1281, 2001

Cobalt alloys

- **Cobalt alloys composition:**
  - Chromium:
    - *Resistance of oxidation, sulfidation*
  - Tungsten:
    - *Strengthen properties*
  - Carbon:
    - *Microstructural carbides for stress abrasion condition*
  - Molybdenum:
    - *Strengthener, enhance resistance to reducing agent*

- **Cobalt alloys Application:**
  - Wear and High temperature
    - Aero and land turbines
  - Biomedical
    - Surgical implant
  - Aqueous Corrosion

Klarstrom D; and all, Cobalt Alloys: Alloying and Thermomechanical Processing, Encyclopedia of Materials: Science and technology, 1279-1281, 2001

Co3O4

Cobalt(II,III) oxide is a dark brown solid with semiconducting properties.

Melting point (1 atm)	895 °C

Figure 3. Flask containing Co3O4 granulate.

Applications:

- *Catalyst*
- Anode material of lithium-ion batteries
- Gas sensor
- A colouring compound in the production of blue glass

Example: Artificial photosynthetic systems has been achieved using nanostructured Co3O4 to catalyze water oxidation under mild conditions.

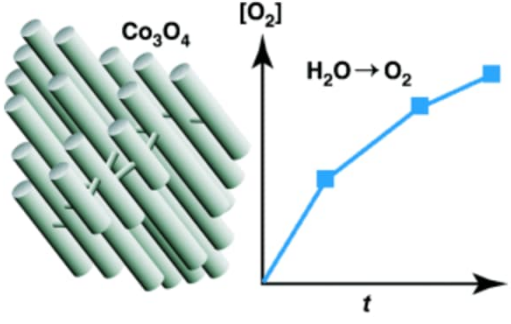


Figure 4. Nanostructured Co_3O_4 in mesoporous silica

The nanorod bundle structure of the catalyst results in a very large surface area, an important factor contributing to the high turnover frequency.

CO3O4 Aalto University Wiki. Available at: https://wiki.aalto.fi/display/SSC/Co3O4 (Accessed: 04 October 2023).
Jiao, F. and Frei, H. (2009) 'Nanostructured cobalt oxide clusters in mesoporous silica as efficient oxygen-evolving catalysts', *Angewandte Chemie International Edition*, 48(10), pp. 1841–1844.

Structure

- Cobalt(II,III) oxide forms a spinel structure
- the oxygen atoms are arranged in a closed cubic packing formation in which the cobalt atoms are contained.
- Cobalt(II) the tetrahedral sites & cobalt(III) the distorted octahedral sites.

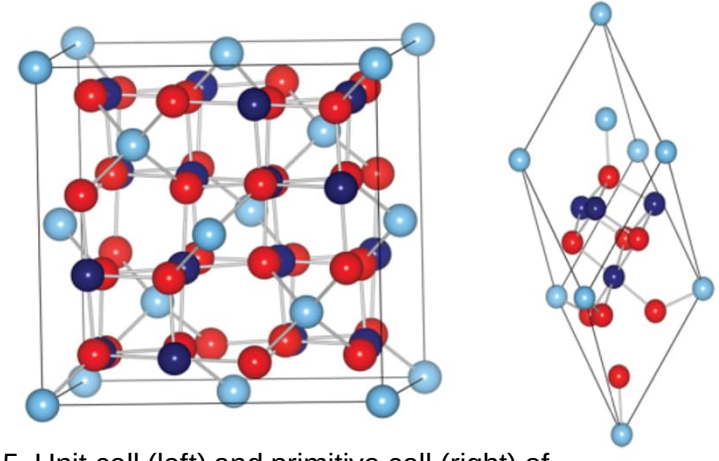


Figure 5. Unit cell (left) and primitive cell (right) of Co3O4. Light cyan and navy blue balls indicate Co2+ and Co3+ ions, red balls indicate O2− ions.

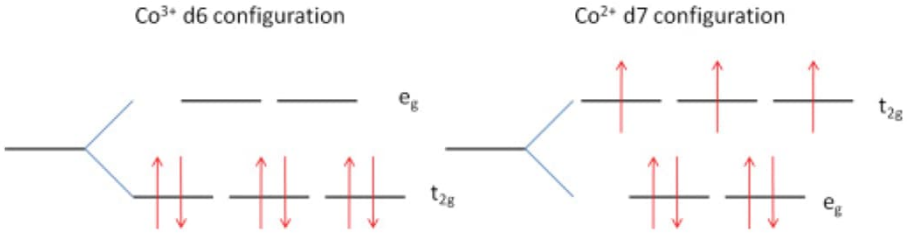


Figure 6. Schematic diagram of crystal field splitting of Co3+ ion in octahedral field (left) and Co2+ ion in tetrahedral field (right).

- Co3+ ions not magnetic
- Co2+ ions carry a magnetic moment.
- Experimentally, Co3O4 is a paramagnetic semiconductor at R.T.
- Becomes antiferromagnetic below TN ~ 40 K
- Weak coupling between nearest neighbor Co2+ ions.

Chen, J., Wu, X. and Selloni, A. (2011) 'Electronic structure and bonding properties of cobalt oxide in the spinel structure', *Physical Review B*, 83(24).

LiCoO2

Discovery:

- A rechargeable lithium battery with a lithium metal anode and a layered TiS2 (transition metal dichalcogenides MX2 (M = transition metal and X = S or Se) cathode in 1976.
- 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.

- The transition metal ion (M^{n}+) that could be in a high oxidation state?
- A higher oxidation state of M^{n}+ *lowers its redox energy* ➡ increase the cell voltage (4V) while also maintaining high electronic conductivity and structural stability.

Why appealing cathod:

- Li+ and Co3+ ions order well in alternate layers.
- the direct Co.Co interaction facilitates high electronic conductivity.
- the interconnected lithium-ion sites support fast lithium-ion conductivity.
- Easy synthesis in ambient air.

Manthiram, A. and Goodenough, J.B. (2021) 'Layered lithium cobalt oxide cathodes', *Nature Energy*, 6(3), pp. 323–323.

Structure

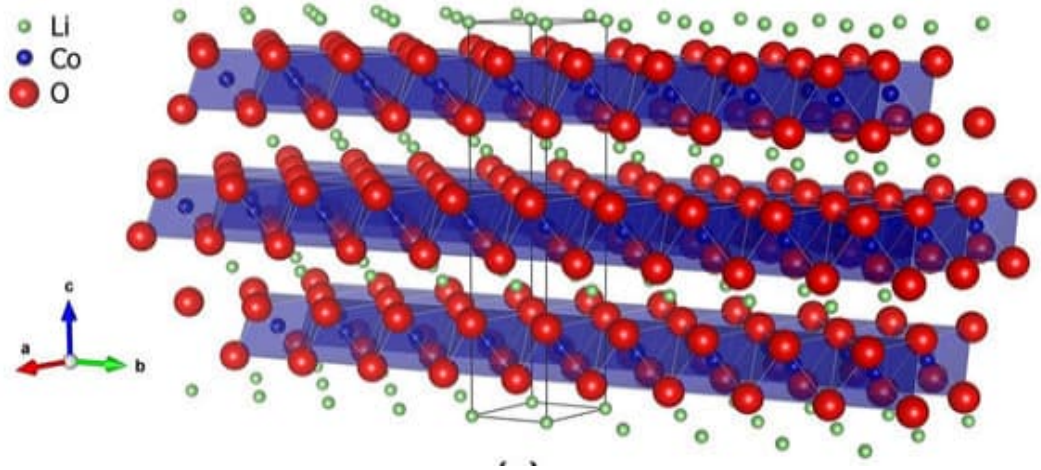


Figure 7. Layered rhombohedral crystalline structure of the LiCoO2.

- The crystal structure consists of closed-packed oxygen layers, with Co and Li ions residing in octahedral sites in alternating layers between the oxygen planes.
- *An ABCABC-type sequential stacking.*

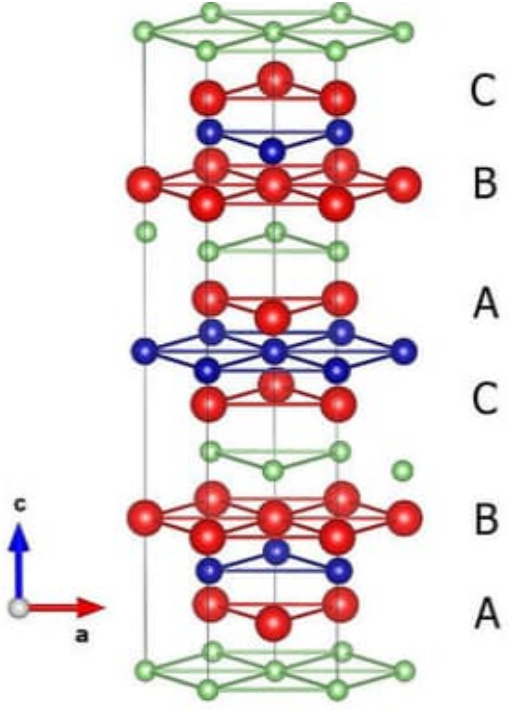


Figure 8. Layered arrangement of the layers.

LICOO2 Aalto University Wiki. Available at: https://wiki.aalto.fi/display/SSC/LiCoO2 (Accessed: 04 October 2023).

Specific Applications

COBALT INSTITUTE (CI) 60 YEARS OF HISTORY

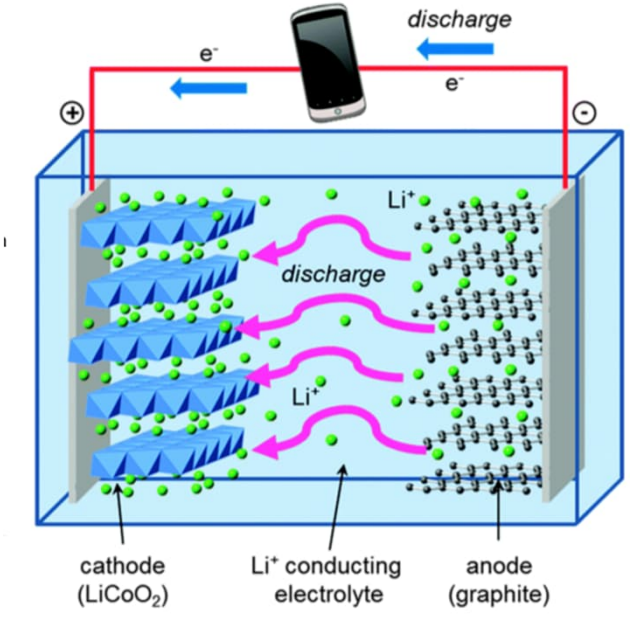
Alloy and Pseucapacitor

- Supercapacitors are electrochemical energy storage devices that store and release energy by reversible adsorption and desorption of ions at the interfaces between electrode materials and electrolyte
- Most common Supercapacitor are based on Carbon material, RuO_2
- New approach: combining carbon material and transition metal => Graphene and amorphous Cobalt Boron Alloy
- Synthesis of nanocomposite of Co-B and graphene by chemical reduction
- Conclusion: nanocomposite of graphene, cobalt and boron alloy has 1,5-fold higher of capacitance than amorphous Co-B alloy, better charge – discharge rate, better stability

Zhang W., et all, Amorphous Cobalt Boron Alloy Graphene Oxide Nanocomposites for Pseudocapacitor Application, Journal of Materials Science & Technology, 33, 438-443, 2017

Cobalt in Lithium-Ion Batteries

- *~ 40%* of global cobalt production is directed toward Li-ion batteries (LIBs)
- Sony Corporation the first rechargeable lithium-ion battery with a graphite anode and a LiCoO2 cathode.
- the limited availability of cobalt
- increase the *Ni content* with appropriate cationic substitutions in layered oxides LiNi0.9Mn0.05Al0.05O2



Electrolyte - a lithium salt in liquid or gel form that provides conduction for the flow of ions.

Manthiram, A. and Goodenough, J.B. (2021) 'Layered lithium cobalt oxide cathodes', *Nature Energy*, 6(3), pp. 323–323.

Cobalt-based electrode materials for sodium-ion batteries

- Cathodes - Combined with rational structure design, *NaxCoO2* is promising
- Anodes - *Cobalt chalcogenides* have the higher conductivities than cobalt oxides do
- Increasing the detail of the electrode design, carbon decoration and nanostructuring, the cycle stability and rate capability can still be improved.

➢ abundant resource of sodium in both the earth's crust and oceans

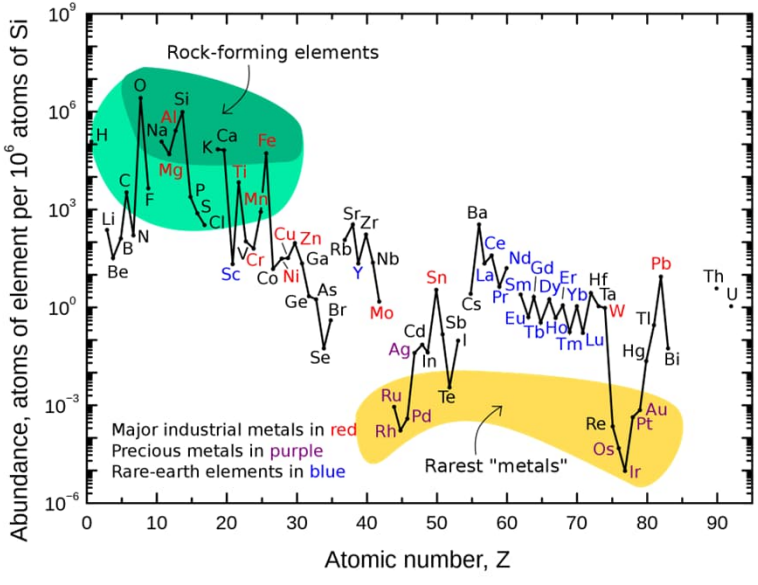


Figure 9. Abundance of elements in Earth's crust (Wikipedia)

Qi, S. *et al.* (2019) 'Cobalt-based electrode materials for sodium-ion batteries', *Chemical Engineering Journal*, 370, pp. 185–207.

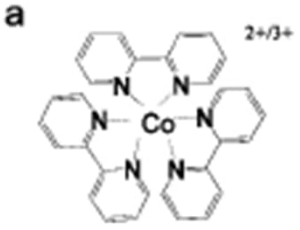
Solar Cell

- Dyes sensitized solar cells are viable alternative to conventional solid state semiconductor device (common solar cell) because they provide the prospect of producing photovoltaic device at low cost and from abundant starting materials.

- Commonly the solar cell used iodide redox couple (I^-/I^-_3), but the goal is to have iodide free solar cell.

- In this case, a cobalt redox couple has developed to replace the iodide which has those properties:
  - -Good stability (photovoltaic/illumination)
  - -Good Redox properties
  - -Soluble in water-based solvent

- Future work: improve potential of the new redox couple, its resistance



cobalt(II)/(III) tris(2,20-bipyridine)

Yum J.H. et all, A cobalt complex redox shuttle for dye-sensitized solar cells with high open circuit potentials, Nat. Commun 3, 631, 2012
Xiang W. et all, Aqueous dye sensitized solar cell electrolytes based on the cobalt(II)/(III) tris(bipyridine) redox couple, Energy&Envi Science, 2012

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Thank you!