Aalto University

# Copper and its chemistry

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## Overview







# Element

Origin - Abundancy - Properties - Production

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### Presentation

- The oldest traces :
  - first half of the 5th millennium BC ,
  - 6 000 years ago : copper ores mining
- Name comes from the Latin cyprium (island of Cyprus)
- 26th most abundant element in the earth's crust (50 ppm)
- Properties :
  - Reddish color
  - very good thermal and electrical conductivity
  - resistant to atmospheric and marine corrosion
  - very malleable, tough and ductile and relatively soft
- Copper ores come in two main chemical forms :
  - Sulphide: CuFeS2, Cu5FeS4, Cu2S --> 80% of world production
  - Oxidised : CuCO3,Cu(OH)2, 2CuCO3,Cu(OH)2, Cu2O



- The element copper, from the ores, is obtained by two metallurgical methods :
  - Pyrometallurgy (sulphide ores)
    - $Cu_2O + FeS = Cu_2S + FeO$
    - $Cu_2S + 3/2 O_2 = Cu_2O + SO_2$
    - $2 \operatorname{Cu}_2 \operatorname{O} + \operatorname{Cu}_2 \operatorname{S} = 6 \operatorname{Cu} + \operatorname{SO}_2$
  - Hydrometallurgy (oxidised or poor sulphide ores)
    - A dissolution
    - Solvent extraction
    - Electrolysis

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### Export and import







Mainly used in :

- Equipment
- Construction
- Transport
- Industry





Electronic configuration – Oxidation state - Reactivity

1	Periodic Table of the Elements															18	
IA 1		Atomic Number															VIIIA 2
Hydrogen	2	None - Symbol										13	14	15 VA	16 VIA	17 VIIA	Helium
Li	Be	Electrons per shell											ć	Ň	ů	F	Ne
Liftium 664 24	Berytlium 20122	State of matter (color of name) Subcategory in the metal-metalleid-nenmetal trend (color of background) Albail metals Albail metals Albail metals Albail metal and albail and and albail an										Boron 10.81 2-3	Carbon 12.011 2-4	Nitropon 14,007 2-5	Crygen 15.997 24	#Buorine 18,998 2-7	Neon 20.180 2-8
Na	Mg	Transition metals											Ši	P	Š	Čl	År
22.16775128 2441	Magnesium 26.335 24.2	3    B	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	Aluminium 26.982 2-8-3	Silicon 28.085 2-5-4	Phosphorus 30,974 2-5-5	Sulfur 32.06 2-8-4	35.45 2.87	39.948 2-8-8
K Potassiwa 37.0443	Ca	Scandium	Titanium 47.847 24.10-2	Vanadium 50,503	Chromium SL9941	Manganese Stratoga	Fe	Cobalt S4 923	Nicket State	Cu Copper \$3346		Gattium 49,723	Germanium 72430	As Arsenic 74,722	Se Setenium 78.971	Br Br Dromine 77.904	Krypton 81779
<sup>37</sup> Rb	<sup>38</sup> Sr	39 Y	<sup>یہ</sup>	Ňb	Mo	43 <b>Tc</b>	Ru	Rh	Pd	Å	<sup>48</sup> Cd	<sup>4</sup> " In	s๊n	si Sb	52 <b>Te</b>	53	Xe
85.4478 245/8451 55	Strontium 17.42 14.1445	Yttrium 88.90584 28-38-9-2	24-8-10-2 72	Niebium 92,90637 2-8-38-12-1 73	Molybdenum 95,95 2-8-10-1 76	(98) 2-6-18-13-2 75	Ruthenium 101.07 2-8-18-15-1	Rhedium 102.91 2-8-38-36-1 77	Palladium 106.42 2-8-18	54/ver 107.87 2-8-18-11	Cadmium 112.41 3-8-18-18-2 8-0	114.82 2-8-18-33	100 118.71 24-18-18-4 82	Antimony 121.76 7-8-8-5	127.60 2-8-18-18-6 8.4	126.90 2-8-18-18-7 8-5	131.29 2-8-18-18-6 8-6
Cs	Ba Barium	57-71 Lanthanides	Hafnium 178.49	Ta Tantalum 100.10705	W Tungsten 183.84	Re Rhenium 186.21	Os Osmium 190.23	Ir Iridium 192.22	Ptatinum	Au Gold 196.97	Hg	TI Thattium 204.38	Pb Lead 2072	Bi Bismuth 208.98	Potonium (201)	At Astatine (210)	Rn
87 Fr	Ra	89-103 Actinides	<sup>104</sup> Rf	<sup>105</sup> Db	<sup>106</sup> Sg	107 Bh	108 Hs	107 Mt	110 Ds	Rg	<sup>112</sup> Cn	<sup>113</sup> Nh	n4 Fl	Мс	Lv	"" Ts	ŬЗ
6220) 2-8-8-32-8-8-1	Radium (25) (+5005+1		Rutherfordium (267) 2-8-16-32-32-16-2	Dubnium (2640 2-8-18-32-32-15-2	Seaborgium (269) 2-8-18-32-32-12-2	8ohrium (276) 2-8-18-32-32-13-7	(277) 24-16-32-32-36-2	Meitnerium (278) 2-8-30-32-32-35-2	Darmstadtium (280) 24-16-32-32-12-1	Roentgenium (282) 2-8-18-32-32-17-2	Copernicium (285) 24-36-32-32-36-2	Nihonium (284) 24-18-32-32-18-3	Flerovium (269) 2-8-18-32-32-18-4	Mascovium (290) 2-8-16-32-32-18-5	(293) 24-16-32-32-16-6	Tennessine (294) 2-8-18-32-32-18-7	Oganesson (294) 24-18-32-32-18-8
		57   a	Ce	Pr	Ňd	Pm	Sm	<b>F</b> u	Ğd	Ťh	μ	Ho	es Fr	Tm	Vh		
		Lanthanum 19851 2419/847	Cenium 14012 2435-19172	Praseodymium 14811 2618-2622	Neodymium 344-24 2-8-922-8-2	Promethium (145) 7-8-18-22-8-2	Samarium 19034 2458-35457	Europium 19196 7-01075-07	Gadelinium 15725 2419-251-2	Terbium 154.52 24.1977422	Dysprosium 142.50 2.618-264-2	Hotmiun 164.93 2418-934-7	Erbium 147.26 2418-354-7	Thutium 168.92 7418-016-2	Ytterblum (73.05 2.636-22.6-2	Lutetium 17457 24/83247	
		Åc	Th	Pa	Ű	Np	Pu	Am	Cm	<b>B</b> k	°	Ës	Fm	Md	No	Lr	
		Actinium (227) 2-8-18-32-18-9-2	Thorium 202.04 24/8-22/8-052	Protactinium 231.04 2-8-18-22-20-8-2	Uranium 238.03 24/8-32-31-9-2	Neptunium (237) 2-8-38-32-32-9-2	Plutonium (244) 2-5-18-32-34-8-2	Americium (243) 248-8-32-25-8-2	Curium (247) 2-8-18-32-25-8-2	Berkelium (247) 2-8-18-32-27-8-2	Californium (250) 24-38-32-28-8-2	Einsteinium (252) 2-6-18-32-29-6-2	C257) 24-8-22-30-8-2	Mendelevium (258) 2-8-8-32-31-8-2	Nobelium (259) 24-96-32-32-8-2	(264) 24-18-25-32-8-3	

### **Electronic configuration**



Exception to the Klechkowski's rule



### **Oxidation states**

- Most common oxidation state +2 (CuCl<sub>2</sub>, CuO, CuSO<sub>4</sub>), less common +1 (CuCl, Cu<sub>2</sub>S, Cu<sub>2</sub>O),
- Can have oxidation state of +3 (KCuO<sub>2</sub>, K<sub>3</sub>CuF<sub>6</sub>) and +4 (Cs<sub>2</sub>CuF<sub>6</sub>),
- **Copper (I) compounds :** cuprous compounds, diamagnetic, colourless, tetrahedral or square planar geometry, more stable state in solid compounds at moderate temperatures
- Copper (II) compounds : cupric compounds, usually coloured, affected by Jahn Teller distortions, more stable state in aqueous solutions

# Metallic and ionic sizes 135pm and 71-87pm Cu $Cu^{2+}$



https:///wwwchem.uwimona.edu.jm/courses/copper.html. https://socratic.org/questions/what-is-the-oxidation-number-of-copper/

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#### Reactivity

- No reaction with water
- Slowly react whit atmospheric oxygen → green layer of verdigris (copper carbonate)
- Protection of the underlying metal from further corrosion = **passivation**
- In the absence of CO2, oxidation in air begins at 120 °C
- Reacts with hydrogen sulphide to form various copper sulphides
- low reactivity + malleability = ideal for architecture





# Compounds

### Properties and Applications

## Compounds of copper in +1 Oxidation

### Cuprous oxide, (Cu<sub>2</sub>O)

- Melting point of 1235 °C, and diamagnetic
- It is used in pigments, fungicides, in rectifier diodes before the use of silicon (due to semiconducting properties)

### Cuprous chloride, (Cu<sub>2</sub>Cl<sub>2</sub>)

- Whitish to greyish solid, moist air converts into greenish color
- Cuprous chloride is used as catalyst in organic reactions, condensing agent for soap and fats

### Cuprous sulfide, (Cu<sub>2</sub>S)

- Occurs in the form of black powder or lumps, and melting point is 1130 °C
- Most used in industries such as luminous paints, solar cells, electrodes and solid lubricants



## Compounds of copper in +2 Oxidation

#### Cupric oxide, (CuO)

- Appear as brownish black powder, with melting point of 1201 °C.
- Used in glass industry, porcelain glazes, and artificial gems. Also use as an oxidation catalyst.

### Cupric chloride (CuCl<sub>2</sub>)

- It is yellowish to brown powder, with 498 °C melting point.
- Use in wood preservative, dyeing and printing of fibers, pigments of glass.

### Cupric sulfate (CuSO<sub>4</sub>)

- It also exist as hydrated form  $CuSO_4 \cdot 5H_2O$  and known as blue vitriol.
- For agriculture purposes, as a pesticides, germicides, soil additive, also in medicines.



## Compounds of copper

### Other compounds of copper

- **ON = +3**: Examples are KCuO<sub>2</sub>
- **ON = +4**: An example is Cs<sub>2</sub>CuF<sub>6</sub>
- Copper acetate Cu(CH<sub>3</sub>COO)<sub>2</sub>
- Copper nitrate Cu(NO<sub>3</sub>)<sub>2</sub>
- Copper oxychloride Cu<sub>2</sub>(OH)<sub>3</sub>Cl
- Copper cyanide CuCN
- Copper bromide CuBr<sub>2</sub>





# Applications

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# Atomic Layer Deposition of Copper Metal Films

# Atomic Layer Deposition of Copper Metal Films

#### ALD of Cu(acac)2 and Hydroquinone Reductant

- Copper has low sensitivity and high resistance to electromigration
- The process of ALD takes place at low temperature
- Band gap of 2.0 eV
- High growth rate of 1.8 Å/cycle

#### Uses

- Microelectronic devices
- Integrated circuits
- Printed circuit boards





30/09/2022 Atomic Layer Deposition of Copper Metal Films from Cu(acac)<sub>2</sub> and Hydroquinone Reductant, Maarit Karppinen and Co/

# Atomic Layer Deposition of Copper Metal Films

#### Improvement of oxidation resistance of copper

- Al<sub>2</sub>O<sub>3</sub> films were deposited by the atomic layer deposition (ALD) technique onto pure copper
- Following Improvements achieved
- Denser structure
- Hardness

#### Applications

- Brightness enhancement films for liquid crystal displays (LCD)
- Micro-lens arrays for antireflective polymer optical films







Improvement of oxidation resistance of copper by atomic layer deposition, M.L. Chang/

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# Reversible coordinative binding and separation of sulfur dioxide in a robust metal—organic framework with open copper sites

### Context

 Challenge : reduce SO2 emissions (anthropogenic sources account for >87% of global emissions)

Development of dry regenerable SO2 sorbents operating under ambient conditions

- First idea : Organometallic structure (MOF) sorbent but reversibility and/or limited stability in contact with highly corrosive SO2
- Second idea : Organometallic structure (MOF) with Open Metal Sites (OMS) : [Cu2(L)] (where L is H4L = 4',4'''-(pyridine-3,5-diyl)bis([1,1'-biphenyl]-3,5- dicarboxylic acid)), named MFM-170.





Structure of H4L (ligand) Structure of MFM-170 from single-crystal X-ray diffraction data

#### • Efficiency of OMS :



Fig. S15. Comparison of SO<sub>2</sub> isotherms up to 1 bar for MFM-170 (black) and MFM-170·H<sub>2</sub>O (red) at 273 K. MFM-170·H<sub>2</sub>O was activated by evacuation at room temperature until the mass was stable. MFM-170 was activated by heating at 423 K under vacuum until the mass was stable.

# Isotherms were measured for the material saturated with MFM- 170·H2O ( no OMS) and MFM-170 ( with OMS° $\,$

The difference corresponds to about twice the density of open Cu(ii) sites (1.46mmolg-1)



30/09/2022 Smith, Gemma L., et al. « Reversible Coordinative Binding and Separation of Sulfur Dioxide in a Robust Metal–Organic Framework with Open Copper Sites ». *Nature Materials*, vol. 18, nº 12, décembre 2019, p. 1358-65. *DOI.org (Crossref)* 

### Properties

• High SO2 adsorption



SO2 adsorption capacity at 298 K and 1.0 bar :

- MFM-170 : 17.5 mmolg-1 at 298 K and 1.0 bar
- MFM-601 : 12.3 mmolg-1
- SIFSIX-1-Cu : 11.0 mmolg-1

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• [Zn2(L1)2(bipy)] : 10.9 mmolg-1 at 293

Strong SO2 adsorption at high temperatures and at low and high pressure (11.6 mmol g-1 at 333 K and 1bar) :



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Smith, Gemma L., et al. « Reversible Coordinative Binding and Separation of Sulfur Dioxide in a Robust Metal–Organic Framework with Open Copper Sites ». *Nature Materials*, vol. 18, nº 12, décembre 2019, p. 1358-65. *DOI.org (Crossref)* 

### Properties

• High thermal and chemical stability

Stable towards heat, water and acidic and basic conditions : no loss of crystallinity or changes in the structure of the material. This is attributed to the unusual connectivity of the structure, where the axially coordinated pyridyl N-donors lock the two cubic lattices and block one of the two axial Cu(ii) sites.



#### • High separation properties

Reversible type I isotherm : MFM-170 can be fully regenerated under varying pressure conditions many times over Efficient separation of SO2 even in the presence of water and at elevated temperatures :



#### • High selectivity

At 1bar and 298K: MFM-170 shows an uptake of : 3.04mmo/g1 of CO2 1.33mmol/g of CH4 0.38mmol/g of CO 0.28mmol/g of N2 (17,5 mmol/g of SO2)



# Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface

### Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface

Hydrophobic Cu dendrite preparation and characterization

- Theorized sustainable energy cycle → relief to numerous environmental concerns and curtail dependency on fossil fuel
- Cycle driven through aqueous CO2 electrolysis
- Cu = efficient and inexpensive catalyst for the CO2 reduction
- Hydrophobic surfaces trap appreciable amount of gas
- Microscale and nanoscale surface structuration





, et al. "Bio-Inspired Hydrophobicity Promotes CO2 Reduction on a Cu Surface". *Nature Materials,* vol. 18, n°11, novembre 2019, p. 1222-27

### Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface

Catalytic activity of hydrophobic and wettable Cu dendrites

- Hydrophobic treatment : submersing dendritic Cu into liquid 1-octadecanethiol
- Without treatment : surface hydrophilic
- Decrease in electrochemically active surface area (ECSA)
- Hydrophobic dendrite : 3,10-3 cm2
- Wettable dendrite : 21 cm2
- Gas trapping → decrease in ECSA

#### Conclusion

- Hydrophobic dendritic Cu → increase in the CO2 reduction selectivity
- Gaseous layer trapped at the surface of the electrode
- Governing factor of CO2 reduction selectivity on Cu



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, et al. "Bio-Inspired Hydrophobicity Promotes CO2 Reduction on a Cu Surface". *Nature Materials,* vol. 18, n°11, novembre 2019, p. 1222-27

## Thank you for your attention

## Questions ?