4. Electrochemistry

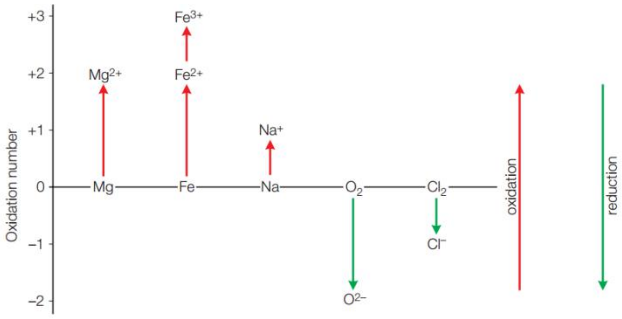
King

考点一：A.Redox

4.3 define oxidation and reduction experimentally and theoretically
4.4 determine the oxidation states (numbers) of individual elements in a compound
4.5 write and balance half reactions and net reactions
4.6 compare oxidation-reduction reactions with other kinds of reactions

1.

The **oxidation number** (or **oxidation state**) tells you how many electrons an atom has donated or accepted to form an ion, or to form part of a compound.



2. Oxidation number rules

- The oxidation number of uncombined elements is **zero**.

$$\overset{0}{Na},\ \overset{0}{C},\ \overset{0}{Cl_2},\ \overset{0}{P_4}$$

- In ions made of just one atom the oxidation number of the element is the **charge on the ion**.

$$\overset{+1}{Na^+},\ \overset{-1}{Cl^-},\ \overset{+2}{Mg^{2+}},\ \overset{-2}{O^{2-}},\ \overset{+3}{Al^{3+}},\ \overset{-3}{N^{3-}}$$

- The sum of the oxidation numbers in a neutral compound is **zero**.

$$\overset{+4-2}{CO_2}$$

- The sum of the oxidation numbers for an ion is the **charge on the ion**.

$$\overset{+6-2}{SO_4^{2-}},\ \overset{-3+1}{NH_4^+}$$

- Some elements have **fixed oxidation** numbers in all their compounds.

1，F 一定是 -1；
2，O 几乎是 -2， 除了H_2O_2； Na_2O_2 (-1)
3，H 几乎是 **+1**，除了和金属结合。(-1)
4, Group1, 2, 3一般是 +1 +2 +3

3. Redox (reduction–oxidation)

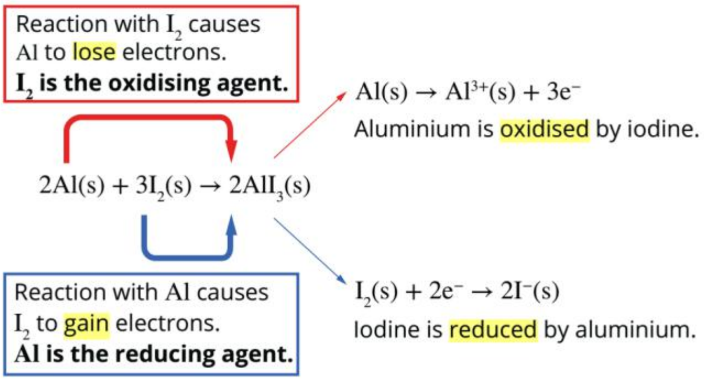
记忆："oil

Reduction: **gaining** of electrons (**decrease** in the oxidation state)

Oxidation: **loss** of electrons (**increase** in the oxidation state)

Reducing agent (reductant): species that **donates electrons** to reduce another reagent. (The reducing agent **get oxidized**.)

Oxidizing agent (oxidant): species that **accepts electrons** to oxidize another species. (The oxidizing agent **gets reduced**.)



3. Half equation

A **half-equation** is used to describe either the gain or the loss of electrons during a redox process.

electron gain (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

electron loss (oxidation): $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Adding together the two half-equations leads to the **full ionic equation**.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Rules for Balancing Oxidation-Reduction Reactions:

1. Write out half-reaction "skeletons."

2. Balance the half-reactions by adding H^+, OH^- or H_2O as needed, maintaining electrical neutrality.

3. Combine the two half-reactions such that the number of electrons transferred in each cancels out when combined.

Examle

Consider the next example:

$Cr_2O_7^{2-} + I^- \rightleftharpoons Cr^{3+} + I_3^-$

The reduction step is given by...

$Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightleftharpoons 2\,Cr^{3+} + 7\,H_2O$

The oxidation step is give by...

$3\,I^- \rightleftharpoons 2\,e^- + I_3^-$

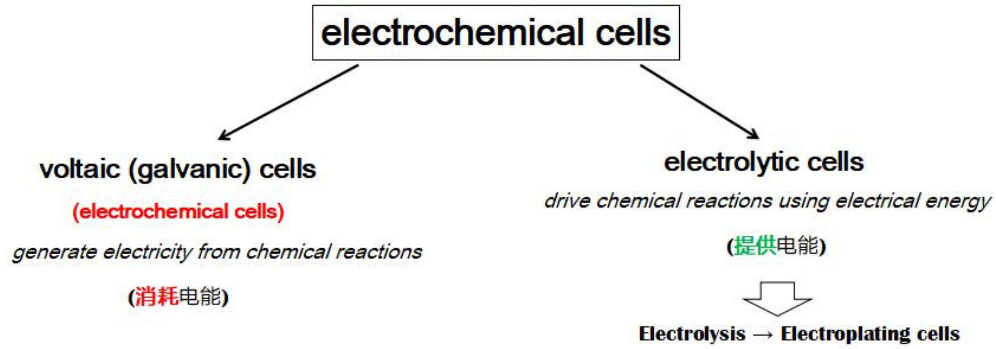
Multiplying the oxidation half-reaction by 3x and adding the two half-reactions together:

$Cr_2O_7^{2-} + 9\,I^- + 14\,H^+ \rightleftharpoons 2\,Cr^{3+} + 3\,I_3^- + 7\,H_2O$

B. Electrochemical cells and Feul cells

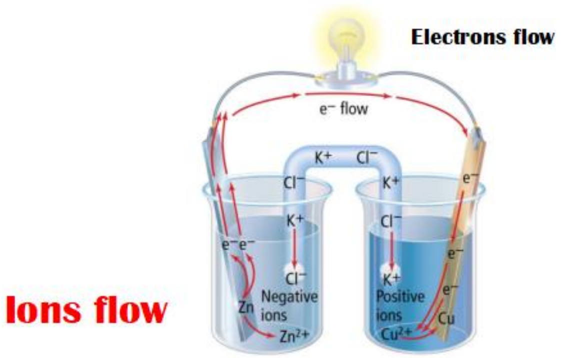
4.1 describe the flow of charge in an electrical circuit
4.2 describe series and parallel circuits involving varying resistance, voltage, and current
4.7 illustrate and label the parts of electrochemical and electrolytic cells and explain how they work
4.8 predict whether oxidation-reduction reactions are spontaneous based on their reduction potentials
4.9 predict the voltage of various electrochemical cells
4.10 compare electrochemical and electrolytic cells in terms of energy efficiency, electron flow/transfer, and chemical change
4.12 explain how electrical energy is produced in a hydrogen fuel cell and a variety of batteries

An **electrochemical cell** is an apparatus that uses a redox reaction to produce electrical energy or uses electrical energy to cause a chemical reaction.

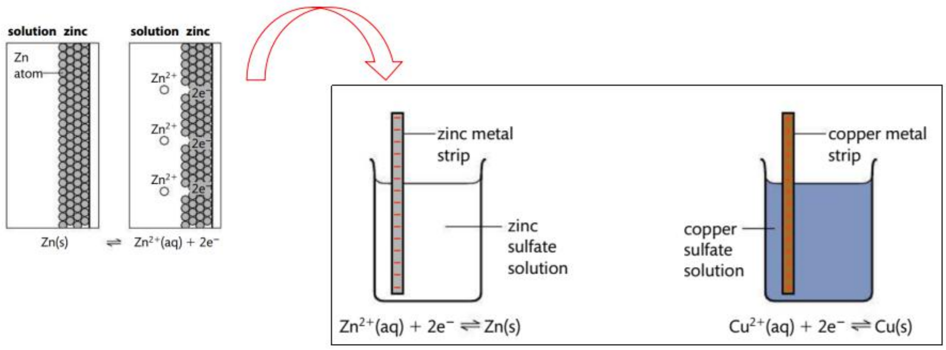


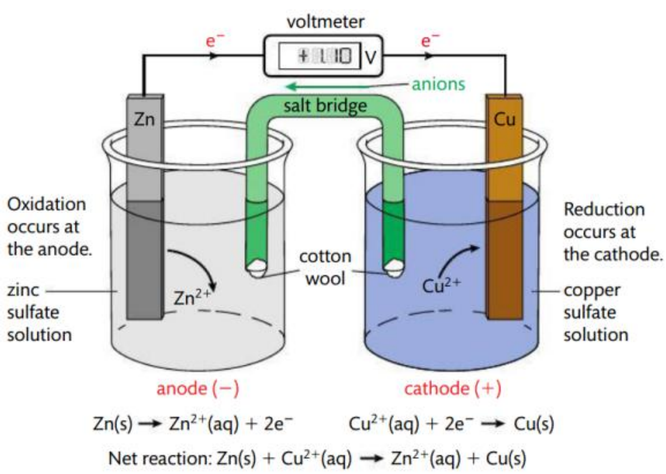
1. Voltaic cell

A **voltaic cell** is a type of electrochemical cell that converts chemical energy to electrical energy by a spontaneous redox reaction.



Zinc atoms form zinc ions by releasing electrons. An equilibrium is set up between the metal and its solution of ions.





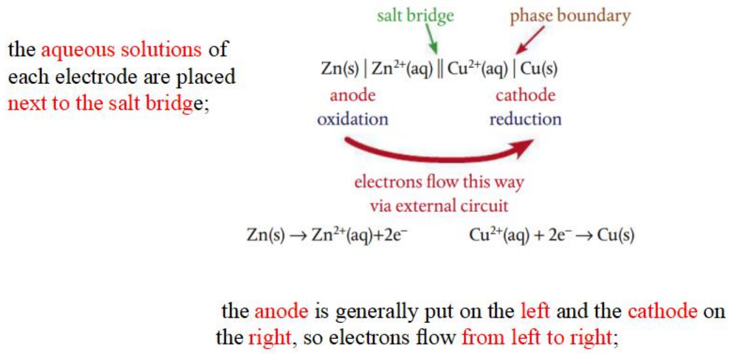
The electrode where oxidation takes place is called the anode.

The cathode is the electrode where reduction occurs

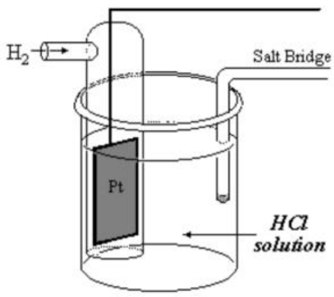
Anode：发生 oxidation 反应，失电子；
Cathode：发生 reduction 反应，得电子；

Redox reactions can be "separated" in a galvanic cell

3. Cell diagram convention



4. Standard Hydrogen Electrode (SHE)

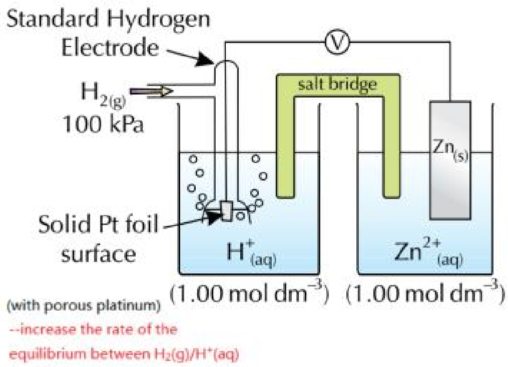


Standard conditions:

- gas pressure, 100 kPa (1 bar)
- temperature, 298 K
- concentration of ions in solution, 1 mol dm^{-3}.

5. Standard electrode potential

The **standard electrode potential, E°** , of a half-cell is the voltage measured under standard conditions when the half-cell is connected to a standard hydrogen electrode.



氢的电势差设定为"零"，

如果能够"吸"氢的电子，定为正的。（**越正越吸**）

如果能够"失"电子给氢，定为负的。（**越负越失**）

越负越(favor)左边

Strong reducing agents
=oxidation

越负越失

HALF-CELL REACTION	E°/V
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.03
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq)$	+0.54
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$\frac{1}{2}Br_2(aq) + e^- \rightleftharpoons Br^-(aq)$	+1.09
$\frac{1}{2}Cl_2(aq) + e^- \rightleftharpoons Cl^-(aq)$	+1.36
$\frac{1}{2}F_2(aq) + e^- \rightleftharpoons F^-(aq)$	+2.87

Strong oxidising agents
=reduction

越正越(favor)右边

越正越吸

6. Potential difference/standard cell difference（电势差）

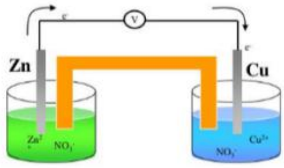
Example: Calculate E⁰ for the cell shown in the Figure below:

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^o = 0.337$ V

$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$ $E^o = -0.763$ V

$$E^o_{Cell} = E^o_{Cathode} - E^o_{Anode} = E^o_{Red} - E^o_{Ox}$$

$$E^o = (0.337) - (-0.763) = +1.10 \text{ V}$$

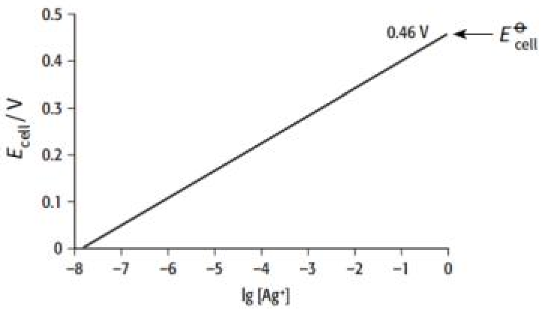


“正减负”

7. Nernst 方程

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s) \quad E^\ominus = +0.46 \text{ V}$$

$$E = E^\ominus + \frac{RT}{zF}\ln\frac{[\text{oxidised form}]}{[\text{reduced form}]}$$



$$E = E^\ominus + \frac{0.059}{z}\log_{10}[\text{oxidised form}]$$

一些“技巧”
如有图:
先判断 anode-cathode
标 electron，ions 流动方向
写反应物/产物。

8. Use Standard Reduction Potentials

Cell potentials can be used to determine if a proposed reaction under standard conditions will be spontaneous.

If the calculated potential is positive, the reaction is spontaneous.

If the calculated potential is negative, the reaction is not spontaneous.

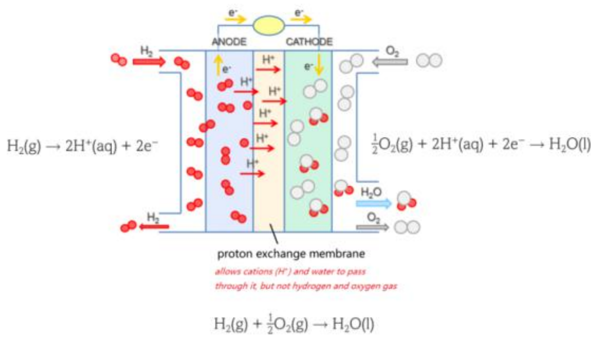
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

“负” “正”

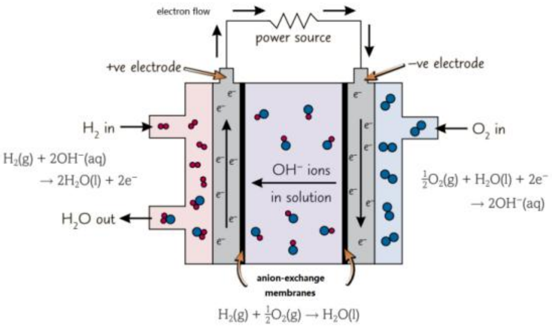
$$E^\ominus_{cell} = E^\ominus_{right} - E^\ominus_{left} = +0.34 - (-0.76) = +1.10\text{V}$$

9. HYDROGEN–OXYGEN FUEL CELL

- In acidic condition:



- In alkaline condition:



C. Electrolytic cells and Electroplating

1. Electrolysis

Electrolysis is the breaking down of a substance using electricity.

An electric current is being passed through a dilute sodium chloride solution, causing water to decompose into **hydrogen gas** and **oxygen gas**

An **electrolyte** is a liquid or solution that undergoes electrolysis

The **electrodes** are made from an inert(unreactive) material.

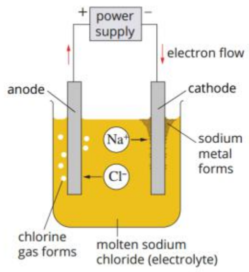
Two inert electrodes, e.g. graphite or platinum

$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

oxidation (loss of electrons)

口诀：红色的猫，一只公牛 –

"RED CAT"; "AN OX"



$Na^+(l) + e^- \rightarrow Na(l)$

reduction (gain of electrons)

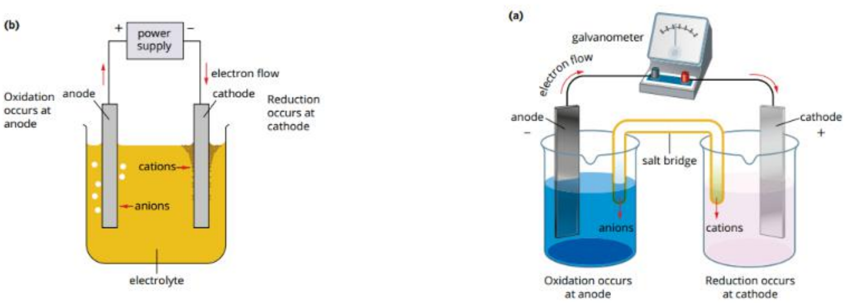
Overall reaction

$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$

*This is a **non-spontaneous reaction**—a reaction that would not occur naturally.*

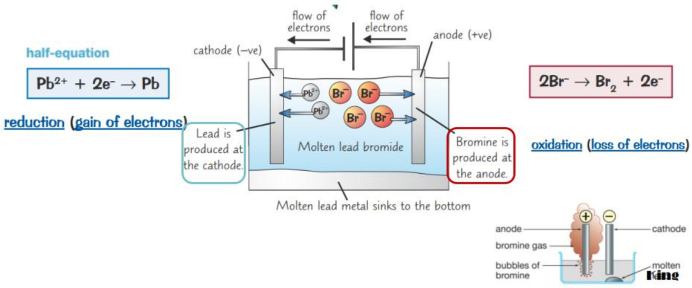
The reverse reaction, between sodium and chlorine, is a **spontaneous reaction**.

2. Electrolytic cells convert **electrical energy** to **chemical energy**, whereas galvanic cells convert **chemical energy** to **electrical energy**.

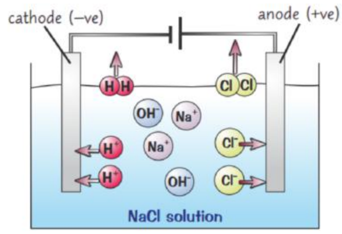


3.

ELECTROLYSIS OF MOLTEN COMPOUND



ELECTROLYSIS OF AQUEOUS SOLUTION



Use the **electrochemical series!!!**

Strongest **oxidising agent**（左上） usually reacts at the **cathode**.

Strongest **reducing agent** （右下） usually reacts at the **anode**.

（**越正越吸**）
（**越负越失**）

	Oxidising agents		Reducing agents		E° (V)
Increasing oxidising strength	$F_2(g) + 2e^-$	⇌	$2F^-(aq)$	Increasing reducing strength	+2.87
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	⇌	$2H_2O(l)$		+1.77
	$Au^+(aq) + e^-$	⇌	$Au(s)$		+1.68
	$Cl_2(g) + 2e^-$	⇌	$2Cl^-(aq)$		+1.36
	$O_2(g) + 4H^+(aq) + 4e^-$	⇌	$2H_2O(l)$		+1.23
	$Br_2(l) + 2e^-$	⇌	$2Br^-(aq)$		+1.09
	$Ag^+(aq) + e^-$	⇌	$Ag(s)$		+0.80
	$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$		+0.77
	$O_2(g) + 2H^+(aq) + 2e^-$	⇌	$H_2O_2(aq)$		+0.68
	$I_2(s) + 2e^-$	⇌	$2I^-(aq)$		+0.54
	$O_2(g) + 2H_2O(l) + 4e^-$	⇌	$4OH^-(aq)$		+0.40
	$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$		+0.34
	$Sn^{4+}(aq) + 2e^-$	⇌	$Sn^{2+}(aq)$		+0.15
	$S(s) + 2H^+(aq) + 2e^-$	⇌	$H_2S(g)$		+0.14
	$2H^+(aq) + 2e^-$	⇌	$H_2(g)$		0.00
	$Pb^{2+}(aq) + 2e^-$	⇌	$Pb(s)$		−0.13
	$Sn^{2+}(aq) + 2e^-$	⇌	$Sn(s)$		−0.14
	$Ni^{2+}(aq) + 2e^-$	⇌	$Ni(s)$		−0.23
	$Co^{2+}(aq) + 2e^-$	⇌	$Co(s)$		−0.28
	$Fe^{2+}(aq) + 2e^-$	⇌	$Fe(s)$		−0.44
	$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$		−0.76
	$2H_2O(l) + 2e^-$	⇌	$H_2(g) + 2OH^-(aq)$		−0.83
	$Mn^{2+}(aq) + 2e^-$	⇌	$Mn(s)$		−1.03
	$Al^{3+}(aq) + 3e^-$	⇌	$Al(s)$		−1.67
	$Mg^{2+}(aq) + 2e^-$	⇌	$Mg(s)$		−2.34
	$Na^+(aq) + e^-$	⇌	$Na(s)$		−2.71
	$Ca^{2+}(aq) + 2e^-$	⇌	$Ca(s)$		−2.87
	$K^+(aq) + e^-$	⇌	$K(s)$		−2.93
	$Li^+(aq) + e^-$	⇌	$Li(s)$		−3.02

2. Rechargeable cells

Cells and batteries use **spontaneous redox** reactions as the source of energy.

When a secondary cell **discharges(放电)**, it acts as a **galvanic cell**, converting *chemical energy* into *electrical energy*

When the cell is **recharged(充电)**, it acts as a type of cell called an **electrolytic cell**.

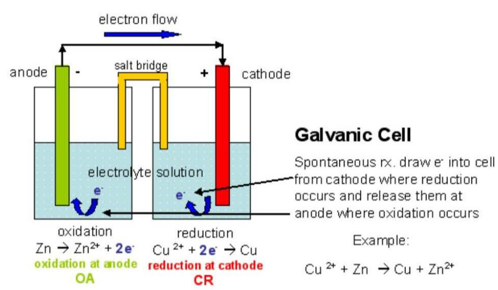
Electrical energy is transformed into *chemical energy* in an electrolytic cell

During the **discharging** process(galvanic cell):

• **oxidation** occurs at the **negative terminal** (the **anode**

• **reduction** occurs at the positive terminal (the **cathode**).

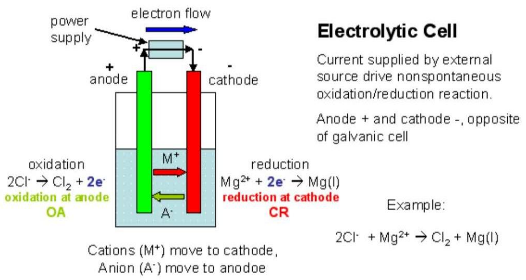
ELECTROCHEMICAL CELLS

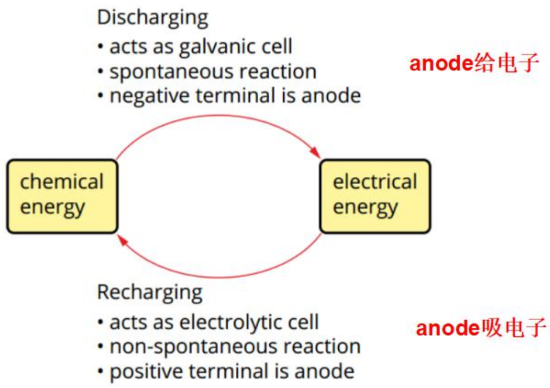


When the cell is **recharging**(**electrolytic cell**), the cell reaction is reversed:

• **oxidation** occurs at the **positive terminal** (the **anode**)

• **reduction** occurs at the **negative terminal** (the **cathode**).





3. Electroplating cells 电镀池