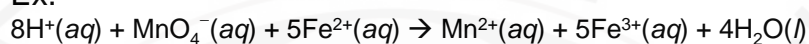# 18 Electrochemistry

The study of the interchange of chemical E and electrical E

※ Galvanic cells [賈法尼]電池
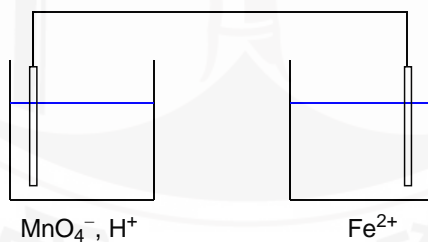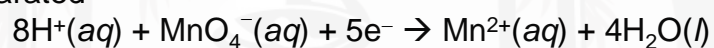
Ex.
$8H^+(aq) + MnO_4^-(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

reduced   oxidized

When directly mixed: only heat formation
no useful work done

If separated
$8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
$5(Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-)$

MnO_4^-, H^+ Fe^{2+}

No e⁻ flow!

Requires a salt bridge or a porous disk for ion flow

e^-

cathode   anode

MnO_4^-, H^+ Fe^{2+}
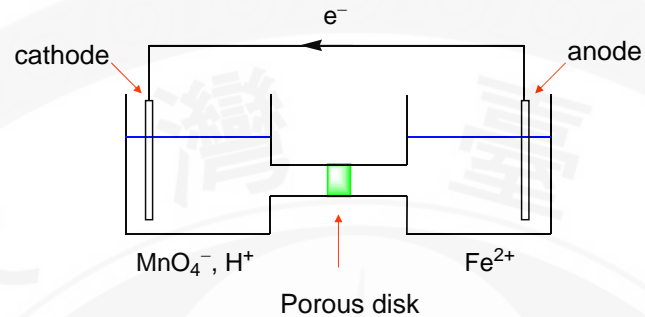
Porous disk

Anion →
Cation ←

Anode: oxidation
Cathode: reduction

Chemical E → Electrical E

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※ Cell potentials (E_{cell})

The driving force of e^- flow
Also called electromotive force (emf)

Unit: volt (V)
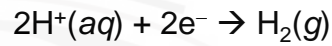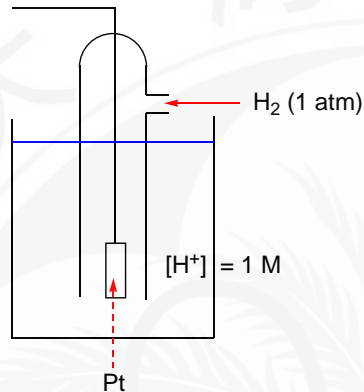1 J of work per coulomb of charge transferred

$$J = C \cdot V$$

※ Standard reduction potentials

No way to measure potentials for half-reactions
⇨ A standard is used for convenience

Standard hydrogen electrode:

H$_2$ (1 atm)

[H$^+$] = 1 M

Pt

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

At standard state of
[H$^+$] = 1 M
P_{H_2} = 1 atm

Assign $E^o_{H^+ \rightarrow H_2}$ = 0 V

Ex. Coupled with Zn(s) → Zn^{2+}(aq) + 2e$^-$
                                       1 M

$$E^o_{cell} = 0.76\ V = E^o_{H^+ \rightarrow H_2} + E^o_{Zn \rightarrow Zn^{2+}}$$

⇨ $E^o_{Zn \rightarrow Zn^{2+}}$ = 0.76 V

A set of half-cell potential can be determined
✓ Reduction potentials are used
✓ Standard state: Solution — 1 M; Gas — 1 atm
       ⇨ standard reduction potential
✓ Potential is an intensive property
    not related to the number of e$^-$
✓ E: concentration dependent
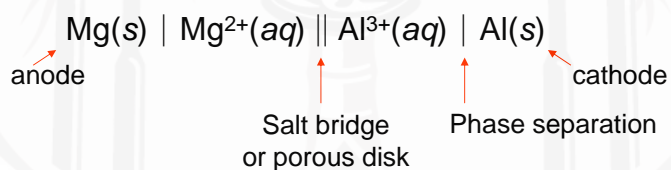
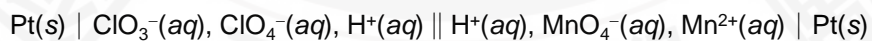Ex.　　$Fe^{3+} + e^- \rightarrow Fe^{2+}$　　　　$E^o = 0.77$ V
　　　　　$Cu^{2+} + 2e^- \rightarrow Cu$　　　　$E^o = 0.34$ V

　　Full reaction:
　　　　$2(Fe^{3+} + e^- \rightarrow Fe^{2+})$　　　$E^o = 0.77$ V
　　　　$Cu \rightarrow Cu^{2+} + 2e^-$　　　　$E^o = -0.34$ V

　$Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$
　　　　　　　　　　$E^o_{cell} = 0.77 - 0.34 = 0.43$ V
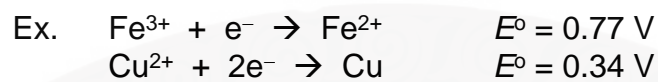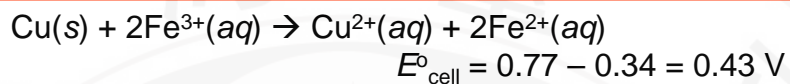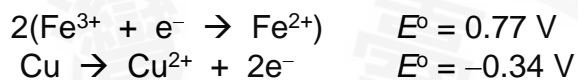
✓ Spontaneous in the positive cell potential direction

◎ Line notation

　　　$Mg(s) \mid Mg^{2+}(aq) \parallel Al^{3+}(aq) \mid Al(s)$
　anode　　　　　　　　　　　　　　　　　cathode

　　　　　　　　　Salt bridge　　Phase separation
　　　　　　　　　or porous disk

Ex.

$Pt(s) \mid ClO_3^-(aq), ClO_4^-(aq), H^+(aq) \parallel H^+(aq), MnO_4^-(aq), Mn^{2+}(aq) \mid Pt(s)$

※ Cell potential,
   electrical work, and free energy

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Work = (Cell potential)(Charge)

J   V   C (coulomb)

From the system's point of view:

$$w = -qV$$

↑ negative   ↑ charge   ↘ cell potential

1 F = charge of 1 mole of e^- = 96500 C

↑ Faraday
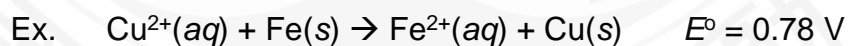
In fact, always accompanied by heat lost

$\because \Delta G = w_{max}$
$\therefore \Delta G = -nFE_{max}$

$\Delta G^o = -nFE^o$ at standard condition

E^o (+) $\Rightarrow$ ΔG^o (−)   spontaneous

Ex. $Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$ $E^o = 0.78$ V

$\Delta G^o = -nFE^o$
$= -(2)(96500)(0.78)$
$= -1.5 \times 10^5$ J

※ Concentration dependence of E

Ex. $Cu(s) + 2Ce^{4+}(aq) \rightarrow Cu^{2+}(aq) + 2Ce^{3+}(aq)$
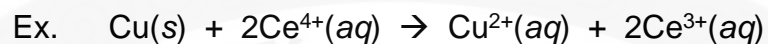
$$E^o = 1.36 \text{ V}$$

Qualitatively

when $[Ce^{4+}]$ ↑   reaction → E ↑

↑

Driving force increases

when $[Ce^{3+}]$ ↑   reaction ← E ↓

$$\Delta G = \Delta G^o + RT \ln Q$$
$$-nFE = -nFE^o + RT \ln Q$$

Nernst equation:

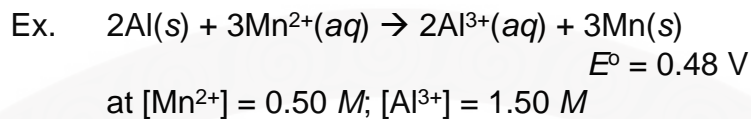$$E = E^o - \frac{RT}{nF} \ln Q$$

In volt (F: 96500 C/mol)

$Q = 1$ $E = E^o$
$Q < 1$ $E > E^o$
$Q > 1$ $E < E^o$

At 25 °C

$$E = E^o - \frac{0.0592}{n} \log Q$$

Ex.　　$2Al(s) + 3Mn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Mn(s)$

$$E^o = 0.48 \text{ V}$$

at $[Mn^{2+}] = 0.50 \; M$; $[Al^{3+}] = 1.50 \; M$

$$E = E^o - \frac{0.0592}{n} \log \frac{[Al^{3+}]^2}{[Mn^{2+}]^3}$$

$$E = 0.48 - \frac{0.0592}{6} \log \frac{[1.50]^2}{[0.50]^3}$$

$$= 0.47 \text{ V}$$
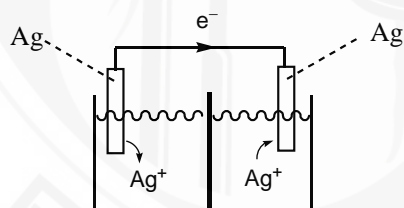
As current flows, concentration change
⇨ E drops
⇨ at equilibrium, $E = 0$, $Q = K$

※ Concentration cell

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0.10 M Ag⁺   1.0 M Ag⁺
0.10 M NO₃⁻   1.0 M NO₃⁻

Overall:
$Ag^+(1.0 \; M) \rightarrow Ag^+(0.10 \; M)$

$$E = E^o - \frac{0.0592}{n} \log Q$$

Q:　$E^o = ?$

Ans.　If $[Ag^+] = 1 \; M$ on both sides
　　　$Q = 1$ and $E = 0$

$$\Rightarrow \quad 0 = E^o - \frac{0.0592}{1} \log 1 \qquad \therefore E^o = 0$$

$$E = 0 - \frac{0.0592}{n} \log \frac{0.10}{1.0} = 0.0592 \quad \longleftarrow \text{ Typically small}$$
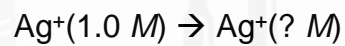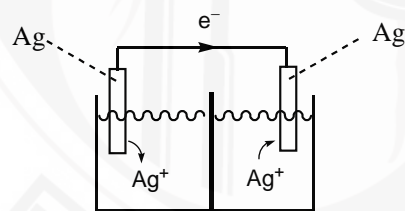
Ex. For cell: T = 37 °C
     Internal cellular fluid $[K^+]_{ICF}$ = 135 mM
     External cellular fluid $[K^+]_{ECF}$ = 4 mM

$$E = E^o - \frac{2.30RT}{nF} \log \frac{[K+]_{ICF}}{[K+]_{ECF}} \qquad (T = 310 \text{ K})$$

$$= -(61.5 \ mV) \log \frac{135}{4}$$

$$= -94 \ mV$$

Application: used to measure ion concentration

Ag ········   ········ Ag

e⁻

Ag⁺   Ag⁺

1.0 M NaCl   1.0 M Ag⁺
sat. AgCl(aq) 1.0 M NO₃⁻

E = 0.58 V

$Ag^+(1.0 \ M) \rightarrow Ag^+(? \ M)$

$$E = 0 - \frac{0.0592}{1} \log \frac{[Ag^+]}{1.0}$$

$[Ag^+] \downarrow \qquad E \uparrow \qquad$ very sensitive

$0.58 = -0.0592 \log[Ag^+]$
$\Rightarrow [Ag^+] = 1.6 \times 10^{-10} \ M$

$K_{sp(AgCl)} = [Ag^+][Cl^-] = (1.6 \times 10^{-10})(1.0) = 1.6 \times 10^{-10}$

$[\ AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \ ]$
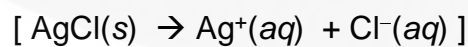
※ More about the intensive property of E

Ex. $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^o = 0.77$ V $\Delta G^o = -(1)FE^o_{Fe^{3+} \rightarrow Fe^{2+}}$
$Cu^{2+} + 2e^- \rightarrow Cu$ $E^o = 0.34$ V $\Delta G^o = -(2)FE^o_{Cu^{2+} \rightarrow Cu}$

$2(Fe^{3+} + e^- \rightarrow Fe^{2+})$ $\Delta G^o = -(2)FE^o_{Fe^{3+} \rightarrow Fe^{2+}}$
$Cu \rightarrow Cu^{2+} + 2e^-$ $\Delta G^o = +(2)FE^o_{Cu^{2+} \rightarrow Cu}$

$Cu(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$
$\Delta G^o_{cell} = -(2)F(E^o_{Fe^{3+} \rightarrow Fe^{2+}} - E^o_{Cu^{2+} \rightarrow Cu})$
$= -(2)FE^o_{cell}$

∴ $E^o_{cell} = E^o_{Fe^{3+} \rightarrow Fe^{2+}} - E^o_{Cu^{2+} \rightarrow Cu}$
⇨   Has no relationship with n

※ Electrolysis of H_2O

Anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^o = -1.23$ V
Cathode $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ $E^o = -0.83$ V

$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$
$E^o = -2.06$ V

‖

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
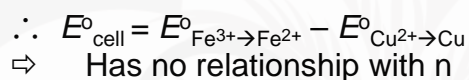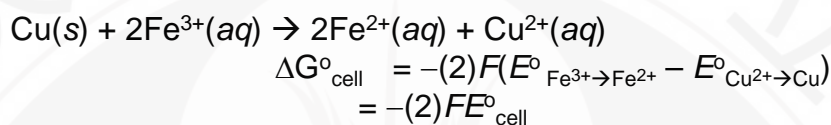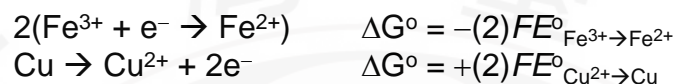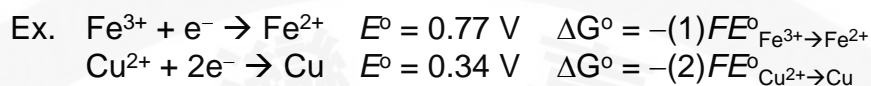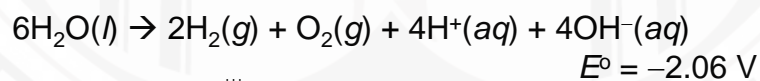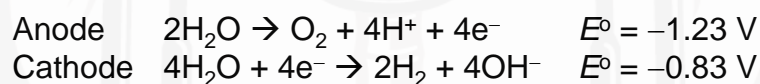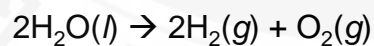
Do we really need -2.06 V?

In pure water, $[H^+] = [OH^-] = 10^{-7}$ M
-2.06 V is based on standard condition:
$$[H^+] = [OH^-] = 1 \ M$$

In fact, $E = -1.23$ V

However, due to over-voltage,
usually needs to be higher than 1.23 V

Over-voltage: due to interface problem of the electrode

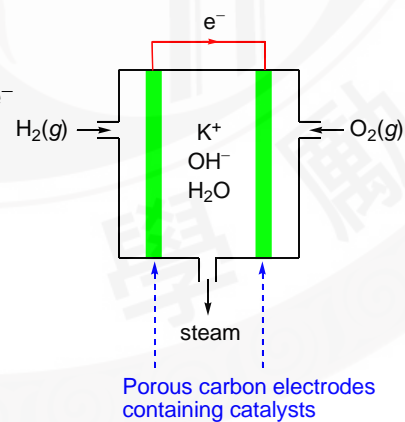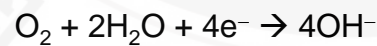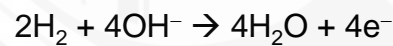Ex. Charging lead storage battery: Pb^o, Pb^{2+}, Pb^{4+} (~2 V)

With Pb electrode: electrolysis of H_2O may occur

With Cd/Pb alloy as electrode: no electrolysis of H_2O

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※ Important areas of research

☆ Photoelectrical water splitting

☆ Fuel cell

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

e^-

$H_2(g) \rightarrow$ K^+ $\leftarrow O_2(g)$
          OH^-
          H_2O

steam

Porous carbon electrodes
containing catalysts

※ 半反應平衡技能：

以葡萄糖($C_6H_{12}O_6$)的氧化為例

1. 先平衡非氧和氫的原子

$$C_6H_{12}O_6 \rightarrow 6CO_2$$

2. 接著以 H_2O 補足氧原子

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2$$

3. 接著以 H^+ 補足氫原子

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+$$

4. 最後以電子平衡電荷

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$$
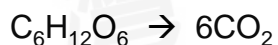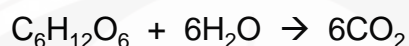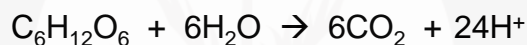
※ Biochemistry

☆ 氧化與還原反應是電子傳遞的重要媒介

有機化合物的氧化還原通常牽涉兩個電子的變化

$$R\text{-}CH_3 \xrightarrow{-2e^-} R\text{-}CH_2OH \xrightarrow{-2e^-} R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}H \xrightarrow{-2e^-} R\overset{\displaystyle O}{\overset{\|}{C}}OH$$

例

$$R\text{-}CH_3 + H_2O \longrightarrow R\text{-}CH_2OH + 2H^+ + 2e^-$$

$$H_3C\text{-}CH_3 + 2\,H_2O \longrightarrow 2\,CH_3OH + 2H^+ + 2e^-$$
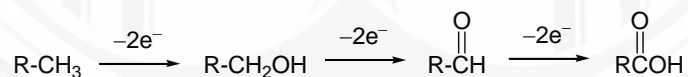
概略上，氧化(例如燃燒)常為釋能的反應
相反的，還原可用為一種儲能的步驟

◎ 透過濃度的差異達成的能量儲藏 (化學位能)

cell memberane

H+
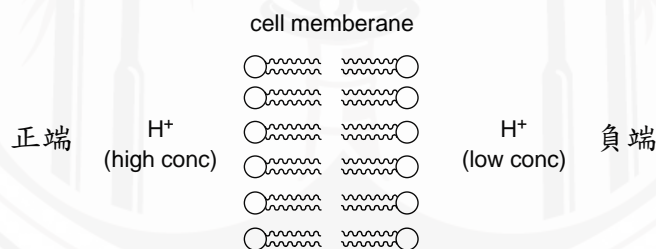(high conc)

H+
(low conc)

H+
(high conc)
$\rightleftharpoons$
H+
(low conc)
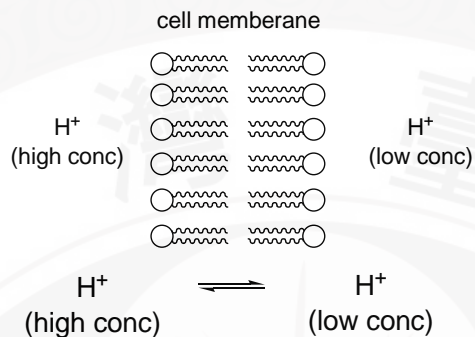
$$\Delta G = \Delta G^o + RT\ln Q = RT\ln \frac{[H^+] \text{ (low conc)}}{[H^+] \text{ (high conc)}}$$

負值
右側能量較低

若濃度比為1/10： $\Delta G = -5.7$ kJ/mol
at T 298 K

◎ 透過電位差異儲存能量 (電位能)

cell memberane

正端   H+
(high conc)

H+
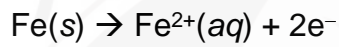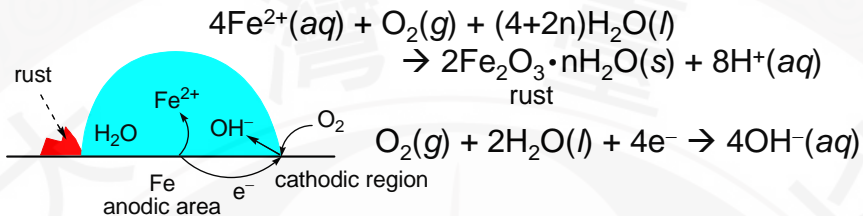(low conc)   負端

有一電位 V_m 存在

當質子進入右側時
$$\Delta G = -nFV_m$$

細胞內外的電位差通常為 0.05~0.2 V (細胞內為負)
→ 0.1 V 儲存約10 kJ/mol 能量
* F = 96500 庫倫/mol；1 庫倫 × 伏特 = 1 焦耳

※ Corrosion

◎ Corrosion of iron

$$4Fe^{2+}(aq) + O_2(g) + (4+2n)H_2O(l)$$
$$\rightarrow 2Fe_2O_3\cdot nH_2O(s) + 8H^+(aq)$$
rust

rust
Fe^{2+}
H$_2$O   OH$^-$ O$_2$
Fe
anodic area   e$^-$ cathodic region

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

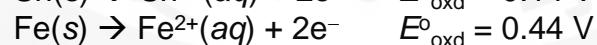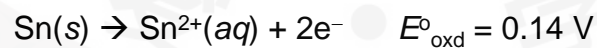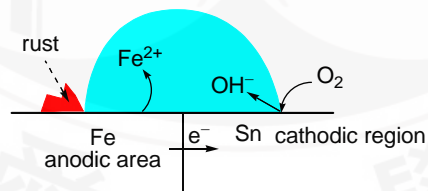$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

- Pit under the dirt but rust formed elsewhere
- Salt serves as good electrolyte
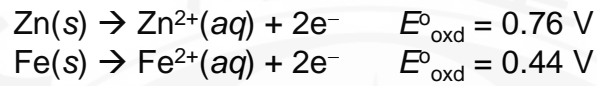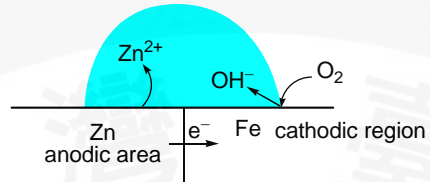 — speeds up the process

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◎ Prevention of corrosion

✓ Apply a coating

- Paint – prevent contact with O_2
- Sn – prevent contact by forming tin oxide layer
  When broken: promotes corrosion by serving as cathode

rust
Fe^{2+}
OH$^-$ O$_2$
Fe
anodic area   e$^-$ Sn cathodic region

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \qquad E^o_{oxd} = 0.14\ V$$
$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \qquad E^o_{oxd} = 0.44\ V$$

Has higher oxidation potential

✓ Galvanized iron – cathodic protection

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^o_{oxd} = 0.76$ V

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $E^o_{oxd} = 0.44$ V

Has higher oxidation potential

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

$E^o_{oxd} = 2.376$ V