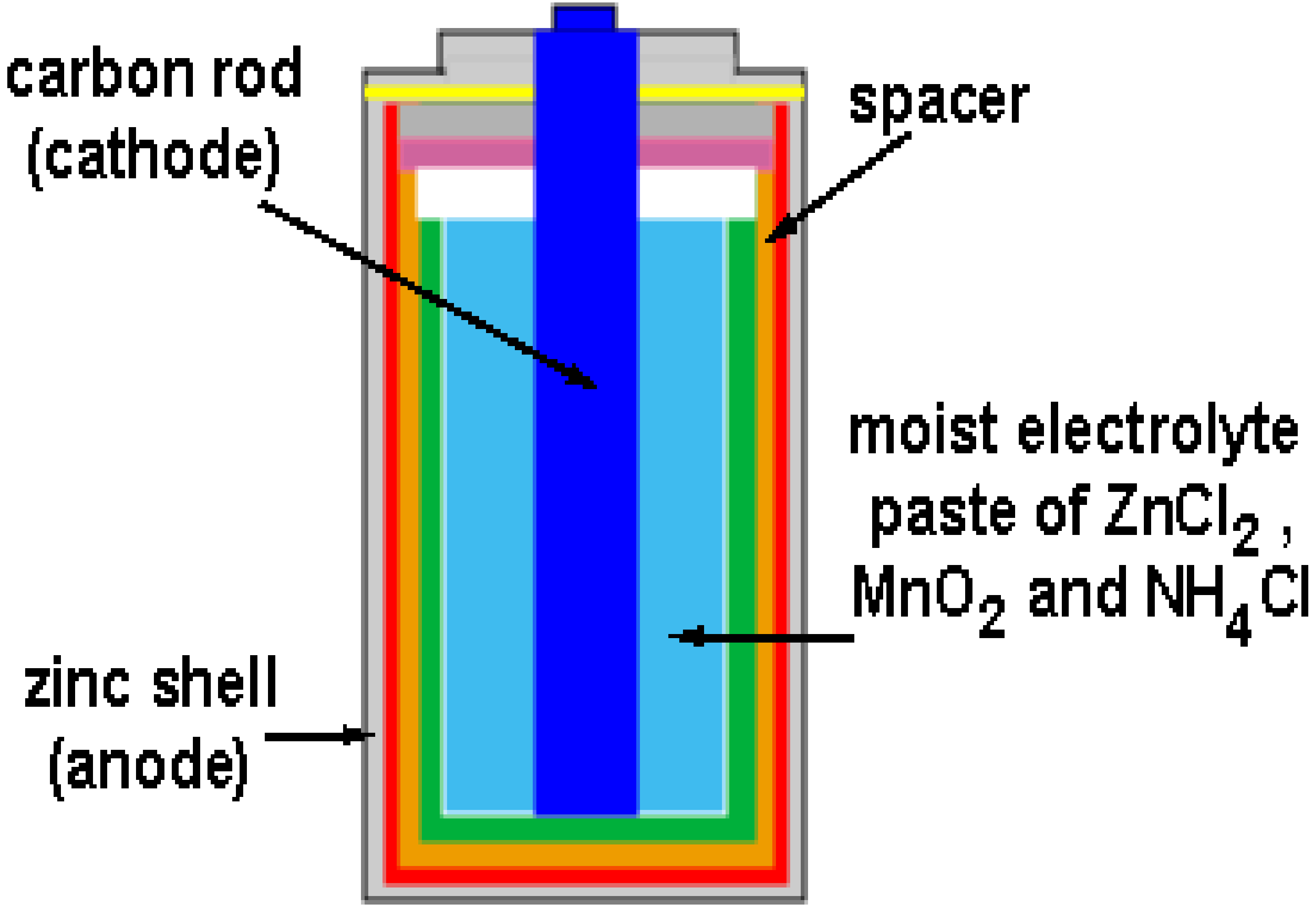
N44 - Electrochemistry

Cells

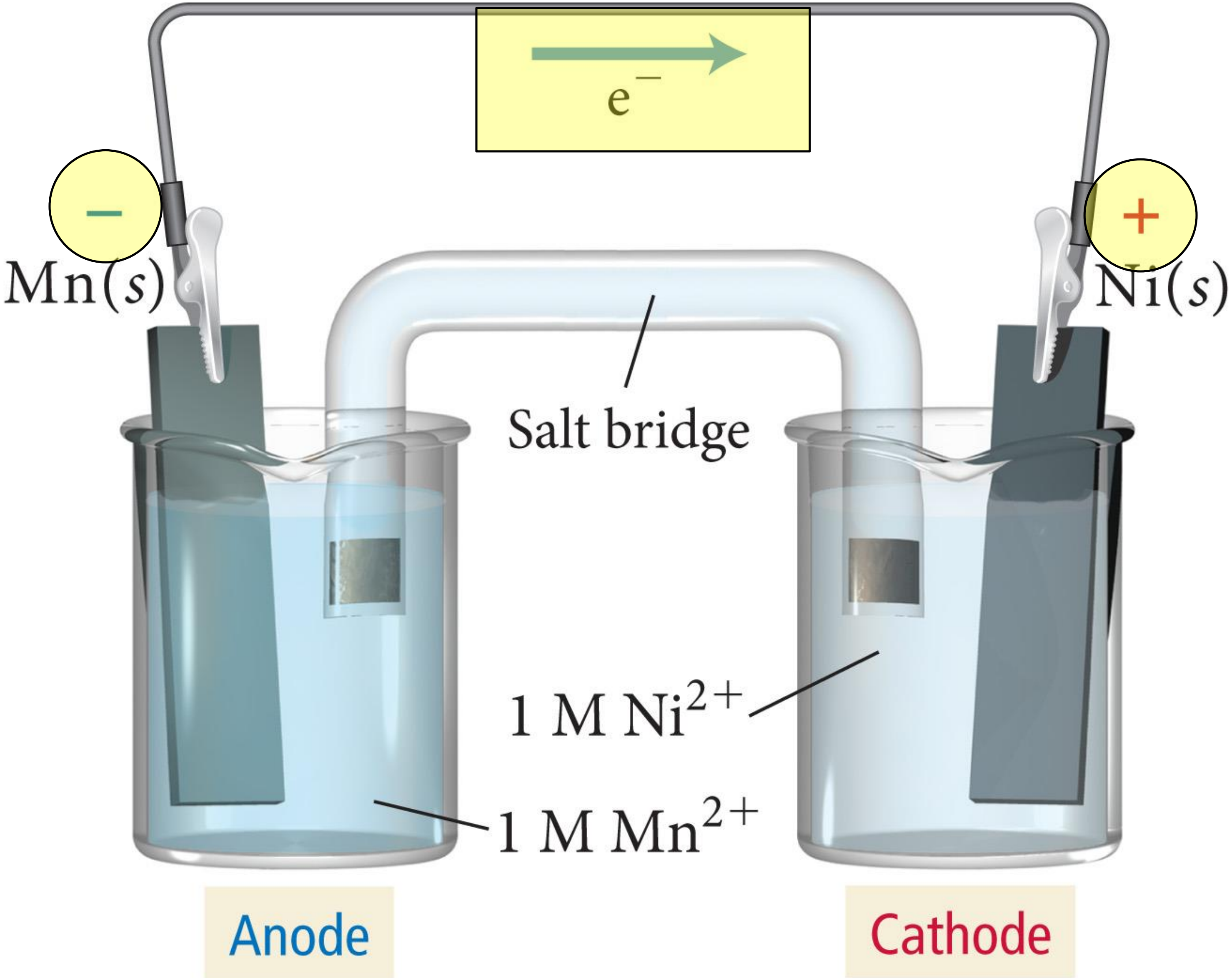


carbon rod
(cathode)
spacer
moist electrolyte
paste of $ZnCl_2$,
MnO_2 and NH_4Cl
zinc shell
(anode)

Direction of Current Flowing

Anode is marked with a (–) sign.
e- are being lost.
They leave and **flow towards the Cathode.**

Cathode is marked with a (+) sign.
e- are being gained.
They are coming from the anode.



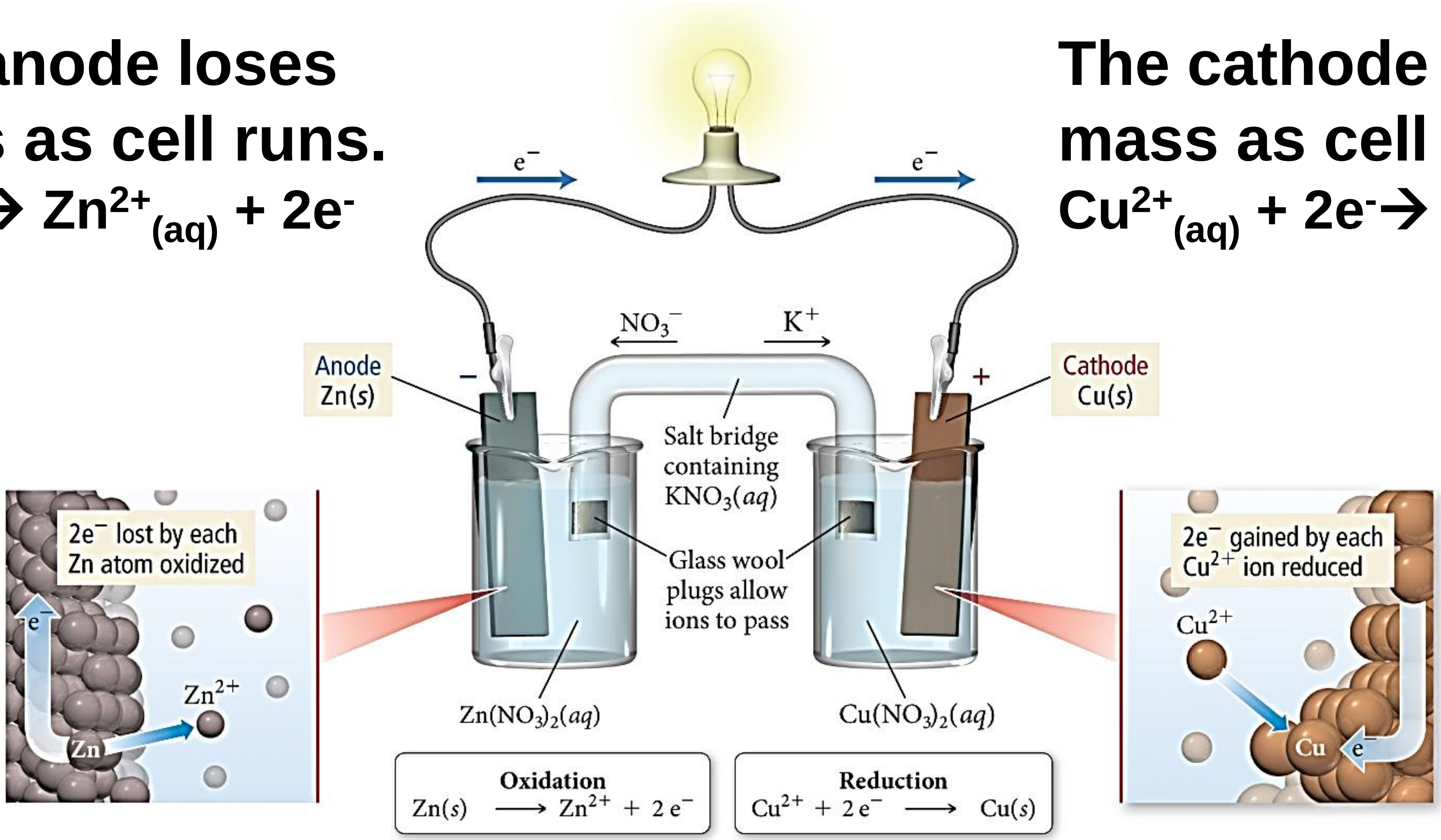
Atomic View

The anode loses mass as cell runs.

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

The cathode gains mass as cell runs.

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

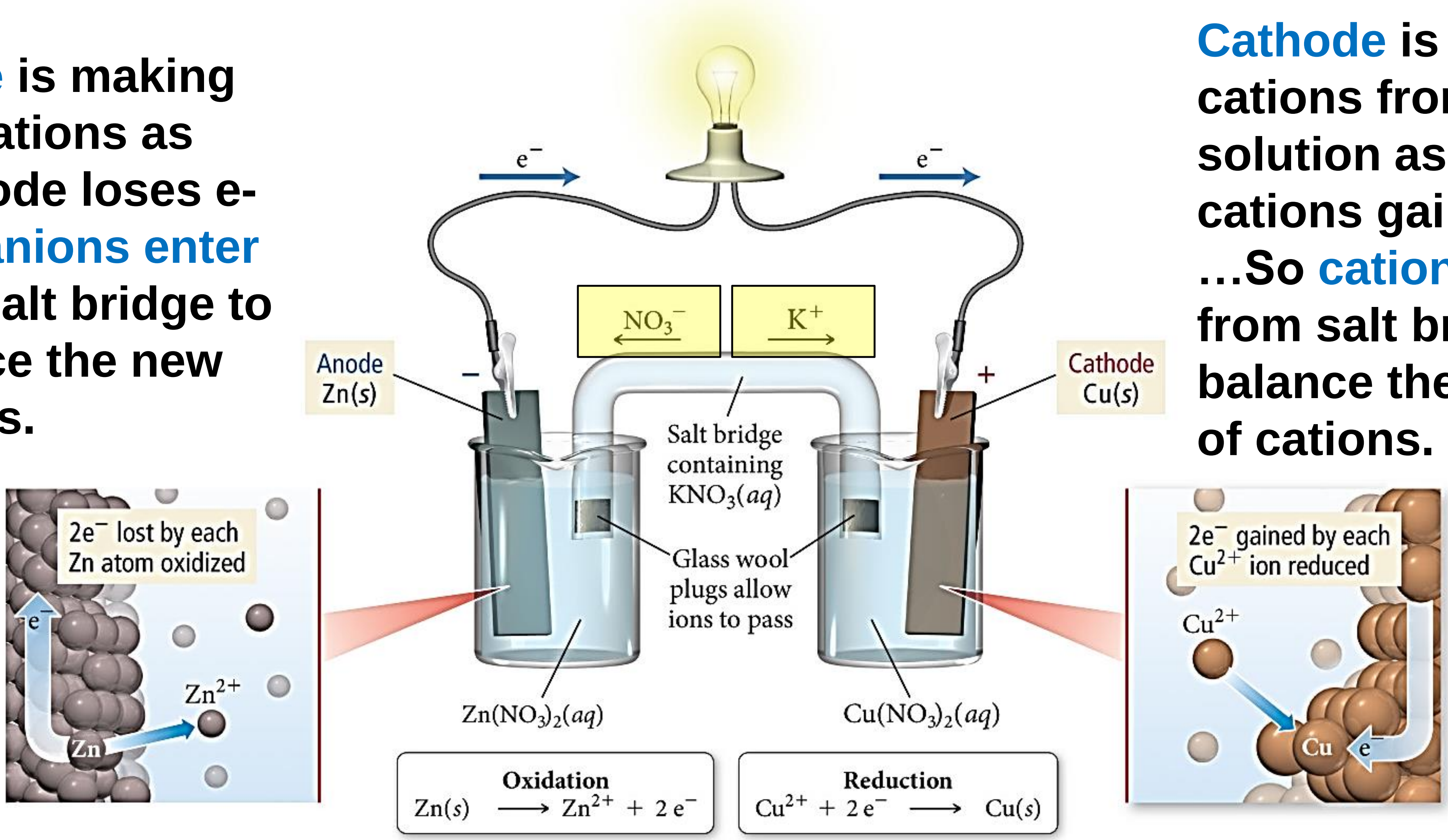


Salt Bridge

Need to keep charges balanced while the cell runs.

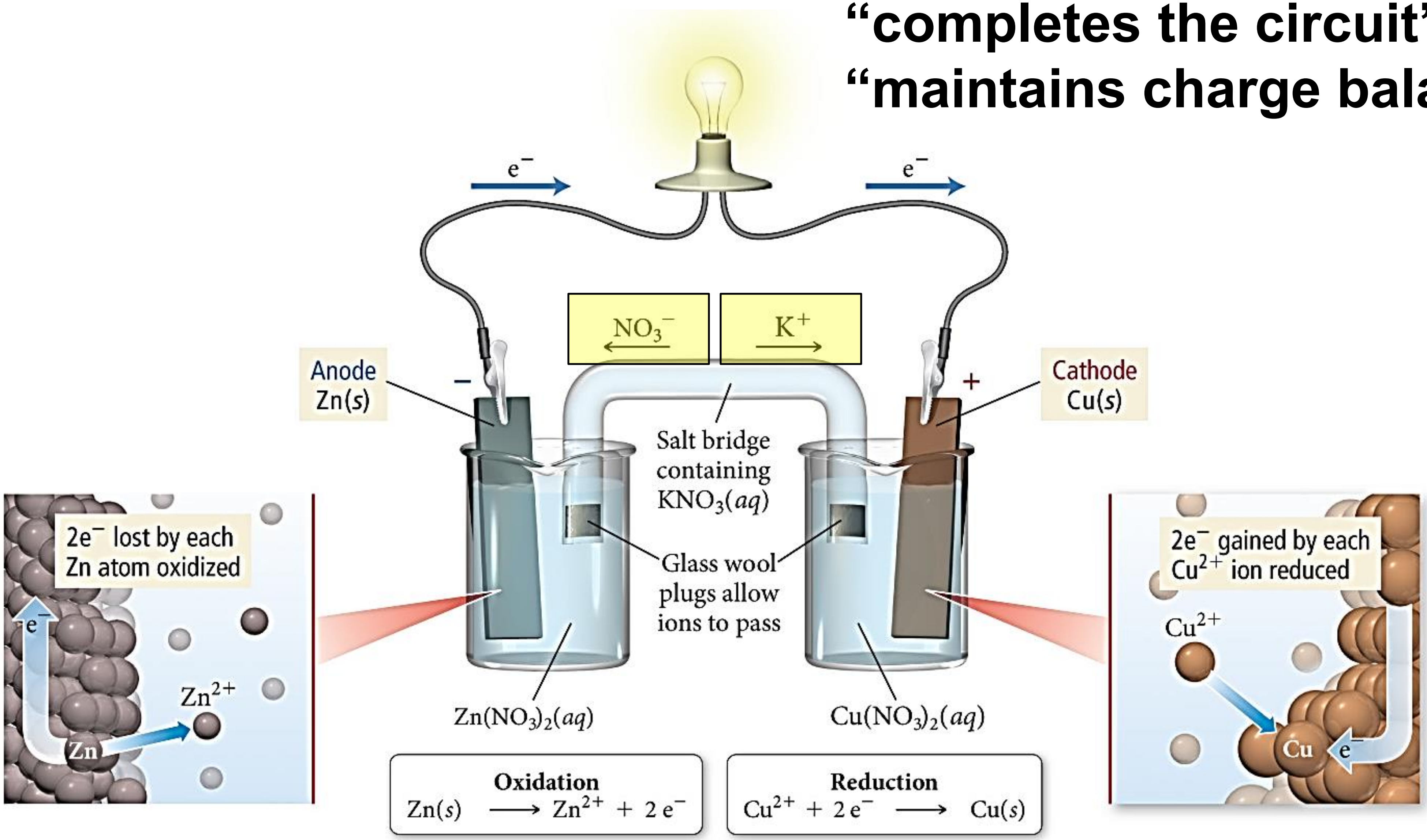
Anode is making new cations as electrode loses e- …So **anions enter** from salt bridge to balance the new cations.

Cathode is losing cations from solution as the cations gain e- …So **cations enter** from salt bridge to balance the loss of cations.



Salt Bridge

We say that the salt bridge "completes the circuit" and "maintains charge balance."



Summary of Electrodes

Anode

- Electrode where oxidation occurs (loss of e^-)
- Anions from salt bridge attracted to it because cations being made.
- Connected to positive end of battery in an electrolytic cell.
- Loses weight in electrolytic cell

Cathode

- Electrode where reduction occurs (gain of e-)
- Cations from salt bridge attracted to it because losing cations.
- Connected to negative end of battery in an electrolytic cell
- Gains weight in electrolytic cell
  - Electrode where plating takes place in electroplating

Galvanic versus Electrolytic Cells

Galvanic

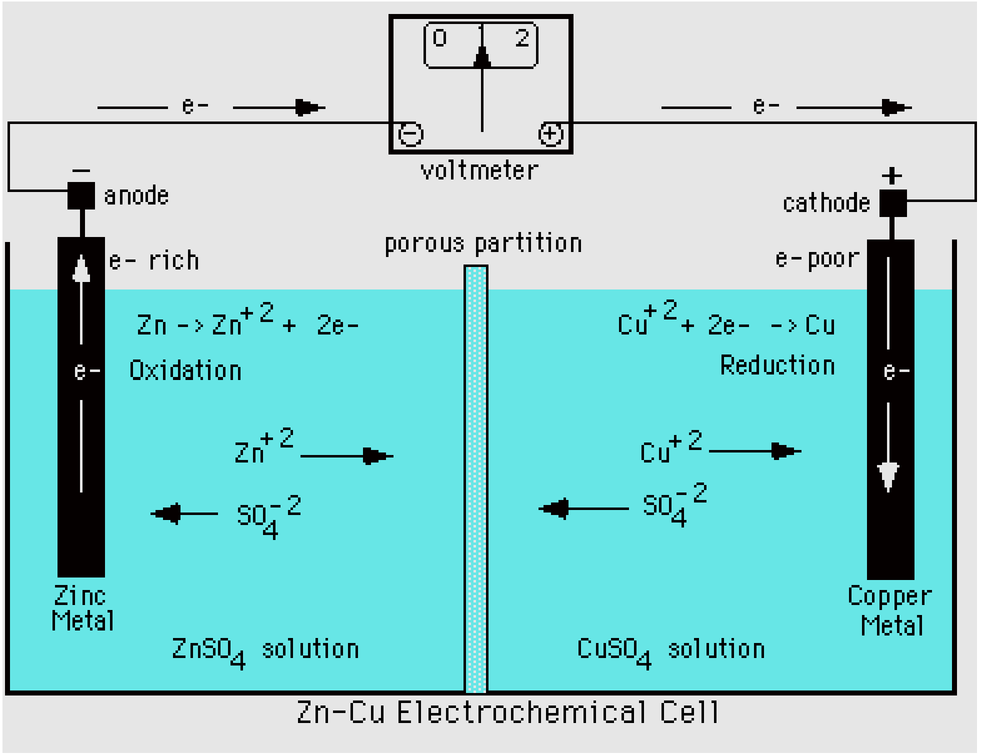
- Converts chemical energy into electrical energy.
- Positive cell potential, $E°_{cell}$ = +
- Spontaneous, negative free energy difference, ΔG = -
- Anode = -   and Cathode = +
- Electrons supplied by the chemical being oxidized.
- Electrons flow from anode to cathode.

Electrolytic

- Converts electrical energy into chemical energy
- Negative cell potential, $E°_{cell}$ = -
- NOT spontaneous, positive free energy difference, ΔG = +
- Anode = +   and Cathode = -
- Electrons supplied by an external source
- Electrons enter from the cathode and come out at the anode.

Galvanic Cell Example Zn - Cu

From a table of reduction potentials:



$Zn^{2+} + 2e^- \rightarrow Zn$ $E = -0.76V$

$Cu^{2+} + 2e^- \rightarrow Cu$ $E = +0.34V$

Cu more positive = reduced

Zn more negative = oxidized

flip eq and sign on E for Zn

$Zn \rightarrow Zn^{2+} + 2e^-$ $E = +0.76V$

$Cu^{2+} + 2e^- \rightarrow Cu$ $E = +0.34V$

$E = (+0.76) + (+0.34) = +1.10\ V$

E = + so galvanic, spontaneous, ΔG = -

Electrolytic Cell Example

A cell is undergoing this rxn:

$$2NaCl \rightarrow 2Na + Cl_2$$

Careful!

Equation is telling you that Na is going from $Na^+ \rightarrow Na$
It is being reduced even though the table shows it would rather be oxidized!!!!
And $2Cl^- \rightarrow Cl_2$ so it is being oxidized even though it would rather be reduced!

$Na^+ + e^- \rightarrow Na$ $\quad E = -2.71V$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $\quad E = 1.36V$

Told that Na^+ = reduced

Told that Cl- = oxidized

flip eq and sign on E for Cl

$Na^+ + e^- \rightarrow Na$ $\quad E = -2.71V$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $\quad E = -1.36V$

$$E = (-2.71) + (-1.36) = -4.07\ V$$

E = - so electrolytic, NON-spontaneous, ΔG = +

Electrolytic Cell Example

A cell is undergoing this rxn:

$2NaCl \rightarrow 2Na + Cl_2$

This cell won't run by itself! You need to hook it up to an outside electrical supply!

$Na^+ + e^- \rightarrow Na$ E = -2.71V

$Cl_2 + 2e^- \rightarrow 2Cl^-$ E = 1.36V

Told that Na^+ = reduced

Told that Cl- = oxidized

flip eq and sign on E for Cl

$Na^+ + e^- \rightarrow Na$ E = -2.71V

$Cl_2 + 2e^- \rightarrow 2Cl^-$ E = -1.36V

E = (-2.71) + (-1.36) = -4.07 V

E = - so electrolytic, NON-spontaneous, ΔG = +

Cell (Line) Notation

Shorthand description of a voltaic cell

Electrode | electrolyte || electrolyte | electrode

Oxidation half cell side ***Reduction half cell side***

- Single | = phase barrier

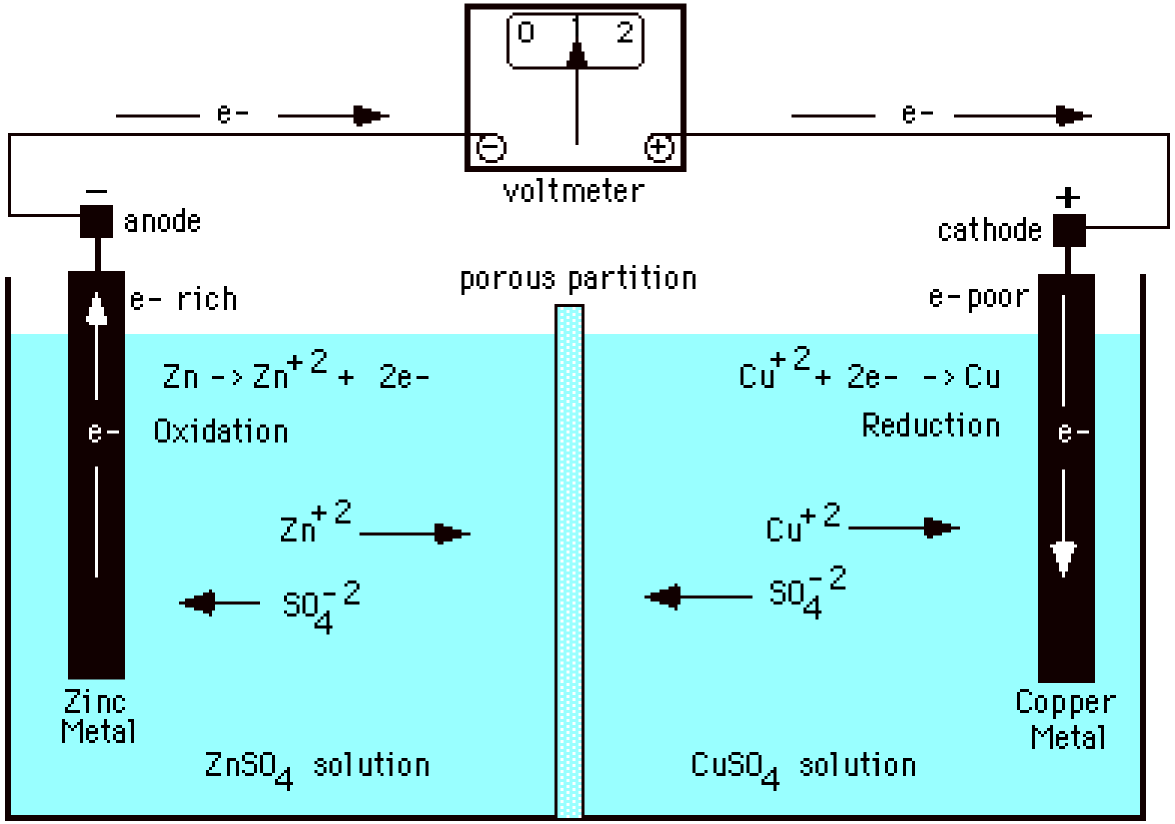
  If multiple electrolytes in same phase, a comma is used rather than **|**

  – Often use an **inert electrode**

  – Sometimes they put the concentrations in also

- Double line || = salt bridge

Line Notation



$$Zn(\mathit{s}) \mid Zn^{2+}(\mathit{aq}) \parallel Cu^{2+}(\mathit{aq}) \mid Cu(\mathit{s})$$

Anode material | Anode solution || Cathode solution | Cathode material