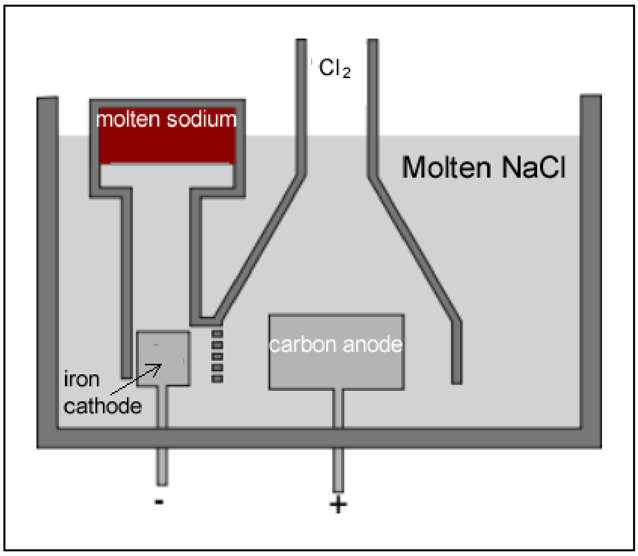
Lesson 2 Electrolysis – aqueous vs molten

Reactive metals that appear below H_2O on the electrochemical series , shown in red on the diagram on the right, are produced using a molten electrolyte.
Aqueous electrolytes are not used because
H_2O is a stronger oxidant than the metal ions of the reactive metals such as K^+, Ca^2, Al^{3+} etc.

$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04

At the cathode, therefore, the following reaction would preferentially take place $2H_2O(l) + 2e \Rightarrow H_2(g) + 2OH^-(aq)$ instead of the reduction of the metal ion.

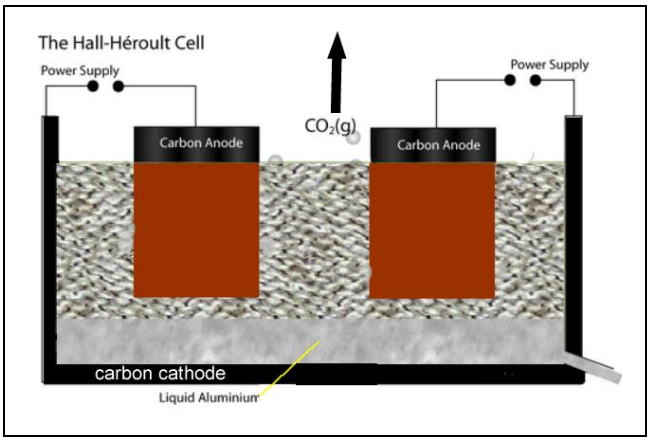
Metals such as Na, Al, and Mg are produced in commercial quantities using molten electrolyte and specialised electrolytic cells.



On the right is a picture of the Downs Cell that is used to produce sodium metal. A high current is maintained which keeps the electrolyte in the molten state.

The reactions that take place are

Cathode	$Na^+(l) + e \Rightarrow Na(l)$
Anode	$2Cl^-(l) \Rightarrow Cl_2(g) + 2e$



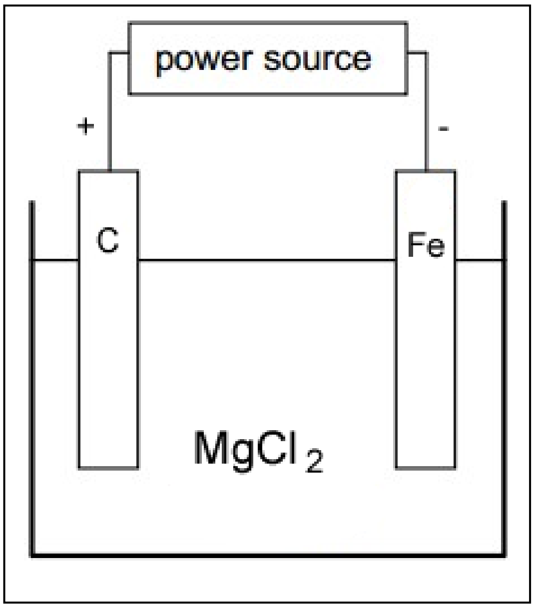
The Hall-Heroult cell, pictured on the right produces pure aluminium. Simply put, it uses molten aluminium (Al_2O_3) in the electrolytic cell.

What is the reaction that occurs at the

cathode	$Al^{3+}(l) + 3e \Rightarrow Al(l)$
anode	$2O^{-2} \Rightarrow 4e + O_2(g)$

The oxygen gas produced at the anode reacts with the carbon anode to produce CO_2 which a green house gas.

1) Magnesium metal is produced in an electrolytic cell. A simplified diagram is shown on the right.



a) Explain whether the electrolyte is aqueous or molten.

The electrolyte must be molten. Water, which is a stronger oxidant than Mg^{2+} must be excluded.

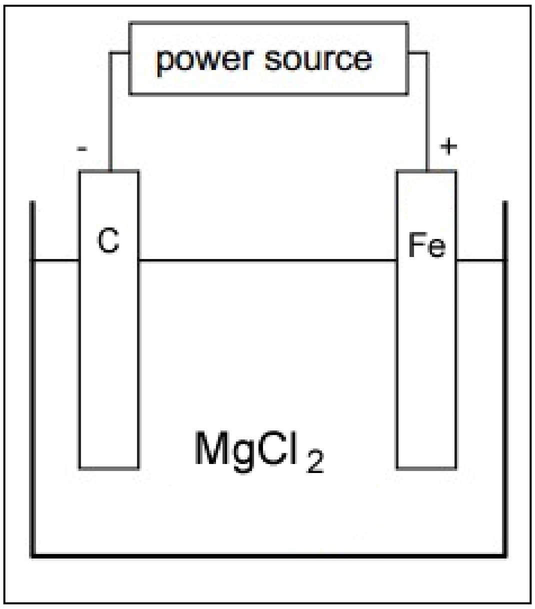
b) On which electrode is the magnesium metal going to form?

Magnesium metal is formed by the reduction of Mg^{2+} to Mg. This is a redcustion reaction which occurs at the cathode (-).

c) What will form at the anode?

Cl_2 gas.

d) The polarity of the electrodes were accidentally changed as shown on the right



i. Explain what would the initial reactions be at each electrode.

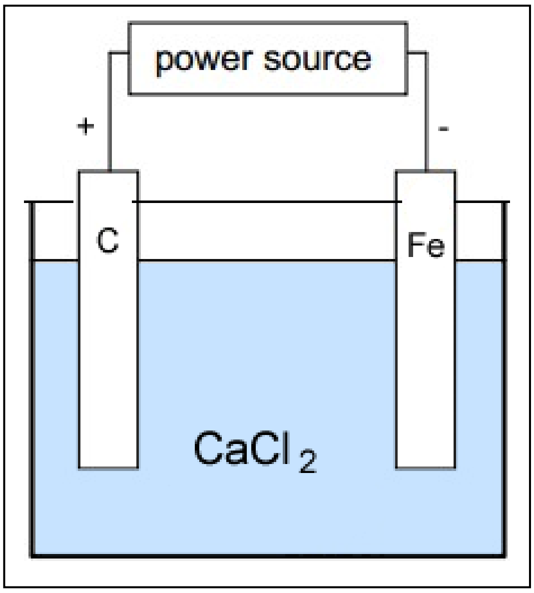
anode $\quad$ *$Fe(s) \Rightarrow Fe^{2+}(l) + 2e$*

cathode $\quad$ *$Mg^{2+}(l) + 2e \Rightarrow Mg(l)$*

ii. Explain how the reactions occurring at each electrode would change over time. Use ionic half equations (states |not necessary)

Overtime, as Fe^{2+} builds up in the electrolyte it will replace Mg^{2+} as the strongest oxidant and will start to deposit at the cathode $Fe^{2+} + 2e \Rightarrow Fe$

2) A student set up the sealed electrolytic cell shown on the right. The aim was to produce calcium metal. A gas was produced at each electrode.



After a while the cell overheated due to a high current and a loud explosion was heard. No smell of Cl_2 was noticed.

a) Was the electrolyte aqueous or molten $CaCl_2$? Explain

Aqueous . Water would react at both electrodes to form oxygen and hydrogen gases.

ii. If the answer to i. was aqueous suggest, with a reason, if the electrolyte was concentrated or dilute?

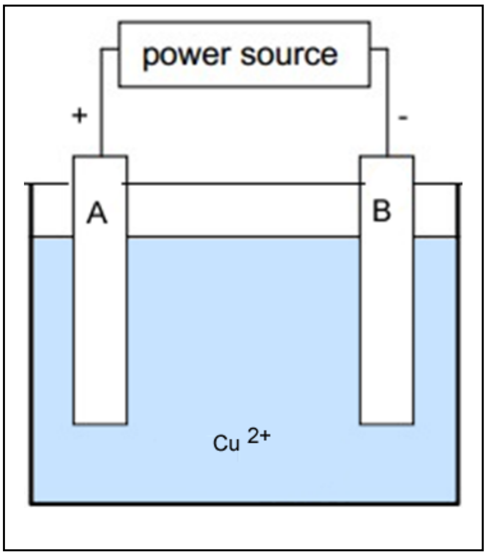
Dilute $CaCl_2$. Probably less than 1 M. Which makes H_2O the stronger reductant present.

b) What was the gas produced at each electrode

anode *oxygen gas*

Cathode *hydrogen gas*

3) The electrolytic cell shown on the right is used by a student to extract copper metal. The electrolyte contains Cu^{2+} and NO_3^- ions in the molten state.



a) Consider the electrodes A and B. Which if any are reactive and which can be inert?

Both electrodes can be inert. At the cathode Cu^{2+} will be converted to Cu and at the anode H_2O will electrolyse into O_2 and H^+.

b) On which electrode will copper metal be deposited?

The reduction reaction $Cu^{2+}(aq) + 2e \Rightarrow Cu(s)$ will occur at the cathode (-). Hence it is electrode "B".

c) It is expensive to use molten $Cu(NO_3)_2$ and the student wishes to minimise costs. Can the student use a solution of $Cu(NO_3)_2$ instead of molten $Cu(NO_3)_2$? Explain

An aqueous solution of $Cu(NO_3)_2$ can be used. Cu^{2+} is a stronger oxidant than H_2O on the electrochemical series.

d) If an aqueous solution of $Cu(NO_3)_2$ is used, what is produced at the anode? Write the equation for the half reaction.

Oxidation occurs at the anode (electrode "A"). Here the strongest reductant will react. In this case it is H_2O

Oxygen gas is produced according to the equation $2H_2O(l) \Rightarrow 4H^+(aq) + 4e + O_2(g)$.

e) In an electrolytic cell using an aqueous electrolyte, electrode "A" is replaced by a solid silver metal electrode. As soon as the electrode is replaced the student noticed that the electrode connected to the negative terminal was not producing the same product as before. A few minutes later the student observed that the other electrode (cathode) is now also producing a different product. Explain the student's observations using the electrochemical series and by writing appropriate balanced equations to the half reactions occurring at each electrode.

Since electrode "A" forms the anode where oxidation takes place the strongest reductant present will react. In this case it is Ag(s) that is the strongest reductant present the reaction that will occur at the anode is $Ag(s) \Rightarrow e + Ag^+(aq)$.

As the cell operates for a while, the concentration of Ag^+ ions builds up to the level where it now interferes with the reaction taking place at the cathode. At the cathode, reduction takes place and it is the strongest oxidant present that will react at the cathode. In this case Ag^+ is the strongest oxidant present and will react according to the equation

$Ag^+(aq) + e \Rightarrow Ag(s)$.

Electrode "B" will be covered with silver metal after several minutes of the cell been in operation.