Lesson 2 Electrolysis – aqueous vs molten

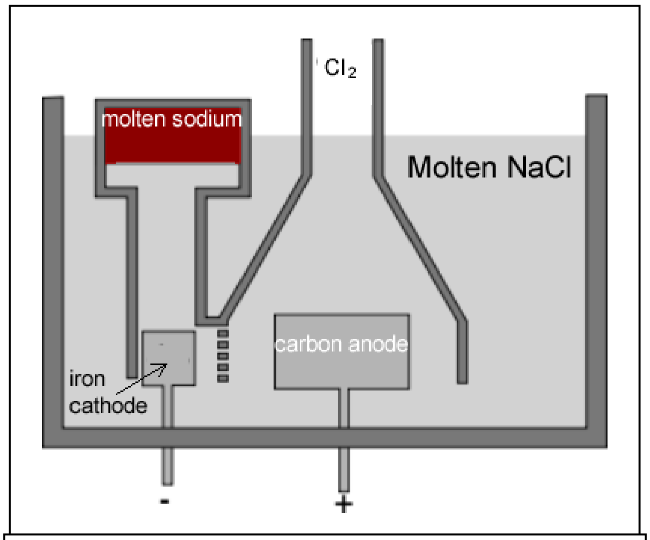
Reactive metals that appear below H_2O on the electrochemical series , shown in red on the diagram on the right, are produced using a molten electrolyte.
Aqueous electrolytes are not used because
H_2O is a stronger oxidant than the metal ions of the reactive metals such as K^+, Ca^2, Al^{3+} etc.

$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−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.

[Click](#) for a revision on predicting half reactions in electrolytic cells

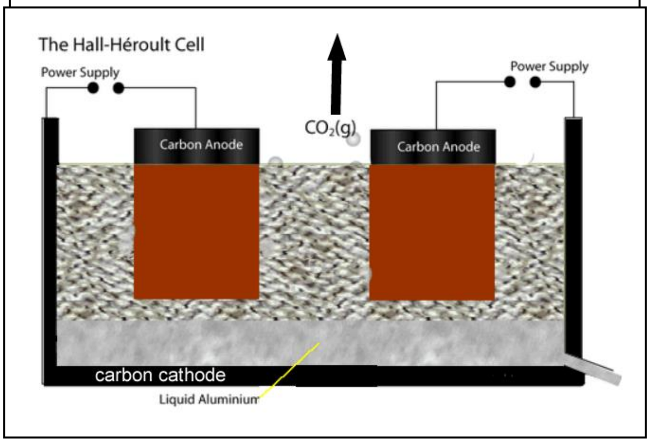


On the right is a picture of the Downs Cell that is used to produce sodium metal. A high current is maintained which keeps the electrolyte in the molten state.

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

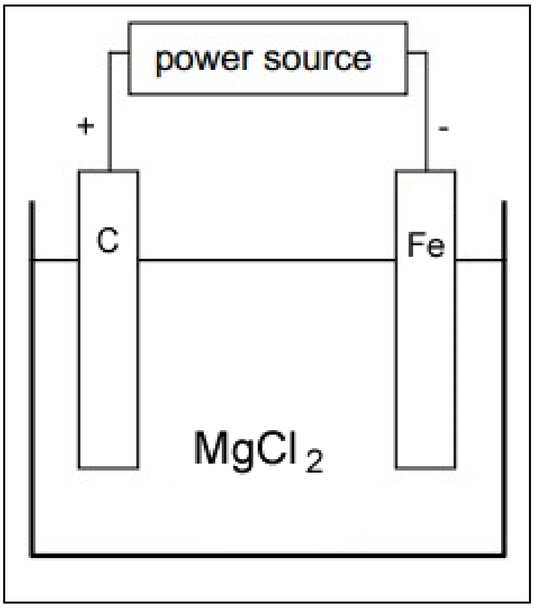
cathode $Al^{3+}(l) + 3e \Rightarrow Al(l)$

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.

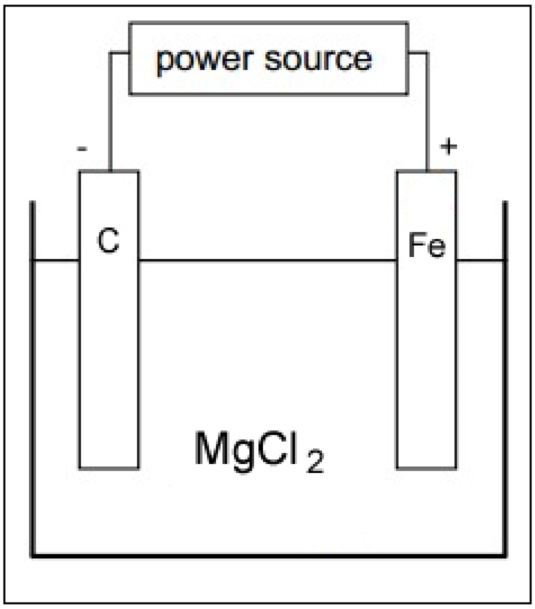


b) On which electrode is the magnesium metal going to form?

c) What will form at the anode?

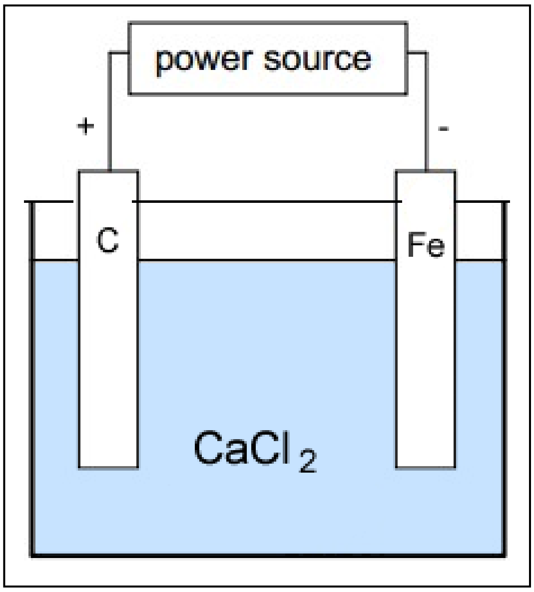
d) The polarity of the electrodes were accidentally changed by the student, as shown on the right

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



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

2) A student set up the sealed electrolytic cell shown on the right. The aim was to produce calcium metal although this was not so successful. A gas was produced at each electrode. After a while the cell overheated due to a high current and a loud explosion was heard.



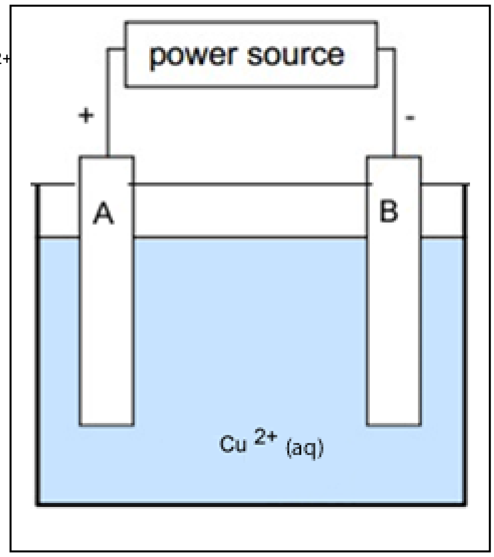
a) Was the electrolyte :

i. aqueous or molten $CaCl_2$? Explain

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

b) What was the gas produced at each electrode

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.



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

b) On which electrode will copper metal be deposited?

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

d) What is produced at the electrode that copper is not deposited on? Write the equation for the half reaction.

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 one of the electrodes was not producing the same product as before. A few minutes later the student observed that the other electrode 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.