Suggested solutions to discussion questions

6 (a) Amt of Ag deposited = 0.100 / 107.9 = **9.27×10^{-4} mol**

(b) $Ag^+(aq) + e^- \rightarrow Ag$
96500 C (1 F) of charge is required to deposit 1 mol of Ag

Amt of Ag deposited = 9.27×10^{-4} mol
Quantity of charge passed = $9.27 \times 10^{-4} \times 96500 = 89.43$ C
Current passed = 89.43 / (30 x 60) = **0.0497 A**

(c) $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$
3 x 96500 C (3 F) of charge is required to deposit 1 mol of Cr

Amt of Cr deposited = $\frac{89.43}{3 \times 96500} = 3.089 \times 10^{-4}$ mol
Mass of Cr deposited = $3.086 \times 10^{-4} \times 52.0$ = **0.0161 g**

7 (a) $Al^{3+} + 3e^- \rightleftharpoons Al$ $\quad E^\ominus = -1.66$ V
$Pb^{2+} + 2e^- \rightleftharpoons Pb$ $\quad E^\ominus = -0.13$ V

Lead has a <u>less negative</u> reduction potential (than aluminium) and so it is <u>relatively easier</u> for its ion to be reduced to the metal. Hence its oxide can be reduced by C.

Aluminium has a <u>very negative</u> reduction potential and so its ion is <u>not easily reduced</u> to the metal. Its ore (e.g. Al_2O_3) cannot be reduced by C and <u>requires electrolysis</u>**.**

Note: Carbon is a cheap raw material (reducing agent). Electrolysis, however, is expensive due to the high electrical power needed to drive the non-spontaneous reaction. As such, reduction by C is preferred. However, for Al^{3+}, reduction by C cannot occur. As such, it has to be extracted from Al_2O_3(ore) via electrolysis. Since Al_2O_3 is insoluble in water, it needs to be in the molten state which adds to the total cost of extraction as the melting process requires high electrical power.

(b) A species with a less positive $E^\ominus$ is more easily oxidised.

$F_2 + 2e^- \rightleftharpoons 2F^-$ $\quad E^\ominus = +2.87$ V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\quad E^\ominus = +1.36$ V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^\ominus = +1.23$ V

$E^\ominus(O_2/H_2O)$ is <u>only slightly less positive</u> than $E^\ominus(Cl_2/Cl^-)$.
A higher $[Cl^-]$ causes $E(Cl_2/Cl^-)$ to decrease, i.e. <u>less positive than +1.36 V</u>.
When concentrated aqueous NaCl (brine) is electrolysed, $[Cl^-]$ is sufficiently high for $E(Cl_2/Cl^-)$ to be <u>less positive</u> than $E^\ominus(O_2/H_2O)$, so that Cl_2 is produced at the anode.

$E^\ominus(O_2/H_2O)$ is <u>significantly less positive</u> than $E^\ominus(F_2/F^-)$.
Though a higher $[F^-]$ causes $E(F_2/F^-)$ to decrease, $E^\ominus(O_2/H_2O)$ will <u>still be less positive</u> than $E(F_2/F^-)$, even for aqueous solution containing a very high concentration of F^-.
If concentrated aqueous sodium fluoride were to be electrolysed, <u>H_2O will still be oxidised in preference to F^-</u>. O_2 will be produced at the anode instead of F_2. Hence, F_2 cannot be produced by the electrolysis of concentrated aqueous sodium fluoride.

Comments
Most students did not realise that the question actually required them to contrast between chloride and fluoride. Simply rehashing that the *E* value of F_2 is more positive than that of chlorine does not earn credit. Stating that there is a "concentration effect" without describing it in greater detail also does not earn credit. In addition, some students compared the wrong *E* values. When we discuss selective discharge at the anode, we should compare the *E* value of F_2 or Cl_2 with that of O_2/H_2O rather than the *E* value of H_2O/H_2.

8 **(a)** From the *Data Booklet*,

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^\ominus = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V
$Ni^{2+} + 2e^- \rightleftharpoons Ni$ $\quad E^\ominus = -0.25$ V

A metal with a more negative (or less positive) $E^\ominus$ value is more readily oxidised.
At the anode, Ni is preferentially oxidised to Ni^{2+} and then Cu is also oxidised (as Ni is a minor impurity) to Cu^{2+} and these ions enter the electrolyte solution. Silver with the most positive $E^\ominus$ value is not oxidised but is collected below the anode as 'anode sludge'.

A metal ion with a more positive (or less negative) $E^\ominus$ value is more readily reduced.
At the cathode, since Cu^{2+} has a more positive $E^\ominus$ value than Ni^{2+}, Cu^{2+} is reduced to Cu and deposits on the cathode as copper metal. Ni^{2+} remains in the electrolyte solution and is not reduced at the cathode.

(b)(i) $Cu^{2+} + 2e^- \rightarrow Cu$
2 x 96500 C (2 F) of charge is required to deposit 1 mol of Cu

Quantity of charge passed = 2.00 x 23.0 x 60 = 2760 C
$n_{Cu} = n_{Cu2+} = \frac{2760}{2 \times 96500} = 0.01430$ mol
Mass of Cu deposited = n_{Cu} x A_r of Cu = 0.01430 x 63.5 = 0.908 g
Increase in mass of cathode is expected to be 0.908 g.

(b)(ii) $n_{Ni2+} = n_{Ni(C4H7N2O2)2} = \frac{mass}{M} = \frac{0.492}{58.7+2(12.0\times4+1.0\times7+14.0\times2+16.0\times2)} = 1.704 \times 10^{-3}$ mol

Mass of Ni oxidised = $1.704 \times 10^{-3} \times 58.7 = 0.100$ g

Mass of Ag = mass of anode sludge = 0.0500 g

Mass of Cu removed = 0.950 – 0.100 – 0.0500 = 0.800 g

9 **(a)** Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Anode: $2Br^- \rightarrow Br_2 + 2e^-$

Comments
- Students need to indicate whether a half equation is a cathode or anode reaction.
- Na^+ will not be reduced at the cathode as $E^\ominus(Na^+/Na)$ is less positive than $E^\ominus(H_2O/H_2)$.
- When writing equations for anode or cathode reactions, you must use a '⟶' sign, **NOT** '⇌' sign.
- The anode is where oxidation occurs, so electrons **must** appear on the product side of the equation. The opposite is true at the cathode.

(b) $S_2O_3^{2-} + 4Br_2 + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Br^-$

Amt of $S_2O_3^{2-} = \frac{35.60}{1000} \times 0.500 = 0.0178$ mol

$2SO_4^{2-} + 10H^+ + 8e^- \rightleftharpoons S_2O_3^{2-} + 5H_2O$
$8Br^- \rightleftharpoons 4Br_2 + 8e^-$

Number of moles of electrons = 8 x 0.0178 = 0.142 mol

Comments
- A number of students are unable to write a correct balanced redox equation as they failed to begin by writing 2 half equations.
- It must be clear in your answer how the mole ratio between $S_2O_3^{2-}$ and electrons was derived.

(c) Since both cells are arranged in series,

$Cr^{n+} + ne^- \rightarrow Cr(s)$

Amt of Cr = $\frac{3.68}{52.0}$ = 0.0708 mol

n = 0.142 / 0.0708 = 2.01 ≈ 2 (whole number)

Comments

- n has to be expressed as a whole number.
- n = amt of electrons / amt of Cr, not the other way round.

10 Number of Cu atoms in 0.1 m length = $\frac{0.1}{3.0 \times 10^{-12}}$ = 3.333×10^{10}

Number of Cu atoms in 0.1 m x 0.1 m electrode = $(3.33 \times 10^{10})^2 = 1.111 \times 10^{21}$

Number of Cu atoms if electrode was coated with a total depth of 2000 atoms (1000 atoms on each side) = $2000 \times 1.111 \times 10^{21} = 2.222 \times 10^{24}$

Amount of Cu atoms if electrode was coated with a total of 2000 atoms = $\frac{2.222 \times 10^{24}}{6.02 \times 10^{23}}$ = 3.691 mol

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

Amt of electrons transferred = 2(3.691) = 7.382 mol

Since $Q = It = n_eF$

$(4.0)(t) = 7.382(9.65 \times 10^4)$

t = 178110 s = $\frac{178110}{3600}$ h = 49.5 h