• Impure copper can be purified by electrolysis, with the impure copper as one electrode and the purified copper as the other. Is the impure copper the cathode or the anode in the electrolysis cell?

Marks 6

The impure copper is the *anode*. As oxidation occurs at the anode, the impure copper is oxidized to give Cu^{2+} , leaving the impurities behind. The Cu^{2+} is then reduced at the cathode to pure Cu(s).

If a battery is used as the power source, is the positive terminal of the battery connected to the impure copper or to the pure copper electrode?

In an electrolytic cell, oxidation at the anode must be forced to occur. This is achieved by making the anode *positive* so that it removes electrons from the reactant (impure copper) at the electrode.

If electrolysis for 1.0 hour with a current of 5.2 A produces 5.9 g of pure copper, calculate the oxidation number of the copper dissolved in the cell.

As the atomic mass of copper is 63.55 g mol⁻¹, 5.9 g corresponds to:

number of moles of copper =
$$\frac{\text{mass}}{\text{atomic mass}} = \frac{5.9 \text{ g}}{63.55 \text{ mol}^{-1}} = 0.093 \text{ mol}$$

A current, I, of 5.2 A applied for a time, t, of 1.0 hour corresponds to:

number of moles of electons =
$$\frac{It}{F} = \frac{(5.2 \text{ A}) \times (1.0 \times 60 \times 60 \text{ s})}{(96485 \text{ C mol}^{-1})} = 0.19 \text{ mol}$$

Each mole of copper therefore requires $\frac{0.19}{0.093} = 2.09$. As the oxidation number is a whole number, this corresponds to an oxidation number of +2.

Oxidation number: +2 (II)

Explain, with the use of standard reduction potentials, why a silver impurity in the copper can be recovered from the cell as silver metal, but a nickel impurity is found dissolved in the electrolyte solution.

The relevant reduction potentials are +0.34 V for $\text{Cu}^{2+}(\text{aq})$, +0.80 V for $\text{Ag}^{+}(\text{aq})$ and -0.24 V for $\text{Ni}^{2+}(\text{aq})$.

For formation of silver metal,

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}(aq)$$
 $E^{\circ} = -0.34 \text{ V (reversed for oxidation)}$
 $Ag^{+}(aq) + e^{-}(aq) \rightarrow 2Ag(s)$ $E^{\circ} = +0.80 \text{ V}$

A voltage of 0.34 V is sufficient to dissolve copper but not to dissolve silver. The silver thus remains as solid Ag(s). The reaction of Ag(s) with $Cu^{2+}(aq)$ is unfavourable as the *reverse* reaction is favourable:

$$Cu(s) + 2Ag^{+}(aq) \Rightarrow Cu^{2+}(aq) + 2Ag(s) E^{\circ} = ((-0.34) + (+0.80)) V = +0.46 V$$

As $E^{\circ} > 0$, the reaction should occur. Silver metal can thus be formed in the presence of copper metal.

For formation of nickel metal,

Cu(s)
$$\rightarrow$$
 Cu²⁺(aq) + 2e⁻(aq) $E^{\circ} = -0.34 \text{ V}$ (reversed for oxidation)
Ni²⁺(aq) + 2e⁻(aq) \rightarrow Ni(s) $E^{\circ} = -0.24 \text{ V}$

The overall reaction is:

$$Cu(s) + Ni^{2+}(aq) \rightarrow Cu^{2+}(aq) + Ni(s)$$
 $E^{\circ} = ((-0.34) + (-0.24)) V = -0.58 V$

As $E^{\circ} < 0$, the reaction will not occur. Nickel metal cannot be formed from Ni²⁺ in the presence of copper metal.

Explain what happens to an iron impurity in the Cu.

The reduction potential for $Fe^{2+}(aq)$ is -0.44 V. Thus, for formation of iron metal,

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}(aq)$$
 $E^{\circ} = -0.34 \text{ V (reversed for oxidation)}$
 $Fe^{2+}(aq) + 2e^{-}(aq) \rightarrow Fe(s)$ $E^{\circ} = -0.44 \text{ V}$

The overall reaction is:

$$Cu(s) + Fe^{2+}(aq) \rightarrow Cu^{2+}(aq) + Fe(s)$$
 $E^{\circ} = ((-0.34) + (-0.44)) V = -0.78 V$

As E° < 0, the reaction will not occur. Iron metal cannot be formed from Fe²⁺ in the presence of copper metal. The iron impurity will stay in the electrolyte solution as Fe²⁺.