Lesson 1- secondary cells

Click to revise secondary cells.

Secondary cells are commonly known as rechargeable batteries. During recharging the cell reactions that occur at each electrode during discharge are reversed producing the original reactants once more. Products formed as the cell discharges must remain in contact with the electrodes if recharging is to take place. During recharging the battery acts as an electrolytic cell converting electrical energy into chemical energy.

During discharge of a battery the cell reactions are spontaneous whereas during recharging the reactions are non-spontaneous.

During discharge the anode, is negative and the place where oxidation takes place, while the cathode is positive and the place where reduction takes place.

Electrons flow from anode to cathode.

During recharge the anode, is positive, while the cathode is negative. The anode is still the place of oxidation while the cathode is still the place of reduction.

Electrons flow from anode to cathode both during recharge and discharge.

During recharge the electrode that was the anode during discharge now becomes the cathode as shown on the right. A voltage greater than the discharge voltage is applied to overcome internal resistance.

Consider the car battery.

During discharge the following reactions take place

<table>
<thead>
<tr>
<th>Anode reaction</th>
<th>Cathode reaction</th>
</tr>
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<tbody>
<tr>
<td>Pb(s) + HSO₄⁻(aq) =&gt; PbSO₄(s) + H⁺(aq) + 2e⁻</td>
<td>PbO₂(s) + HSO₄⁻(aq) + 3H⁺(aq) + 2e⁻ =&gt; PbSO₄(s) + 2H₂O(l)</td>
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Battery life.

The life of the battery becomes reduced as products and reactants of the reactions taking place become detached from the electrode. Temperature also plays a critical role in the life of a battery. High temperatures can severely reduce the life of a battery by accelerating side reactions which do not produce current. Side reactions may involve the removal of reactant or electrolyte or speeding up the corrosion of electrodes. Low temperatures, however, slow reaction rates and hence decrease the current supplied by the battery.
1) A rechargeable galvanic cell, based on nickel and cadmium (NiCd cell), has been commercially available for a number of years and has been used to power small appliances such as mobile phones.

The overall cell reaction for the alkaline cell when discharging is:

\[ \text{Cd(s)} + 2\text{NiO(OH)(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)\textsubscript{2}(s)} + 2\text{Ni(OH)\textsubscript{2}(s)} \]

i. What feature of this secondary cell enables it to be recharged?

The products formed at the anode and cathode remain in contact with the electrodes.

ii. Give the equation for the half reaction that takes place at the negative electrode when the cell is discharging. Keep in mind it is an alkaline cell.

Write the half equation as though it takes place in an acid environment then remove the H\(^+\) by adding OH\(^-\) to both sides:

\[ \text{Cd(s)} + 2\text{OH}^- (aq) \rightarrow \text{Cd(OH\textsubscript{2}}(s) + 2\text{e}^- \]

iii. Give the equation for the half reaction that takes place at the electrode connected to the negative terminal of the power supply when the cell is recharging. The negative terminal during recharging is the cathode where reduction takes place. This will be the reverse of the oxidation reaction that takes place during discharge.

\[ \text{Cd(OH\textsubscript{2}}(s) + 2\text{e}^- \rightarrow \text{Cd(s)} + 2\text{OH}(aq) \]

2) A galvanic cell is set up as shown on the right with a voltmeter.

a) Indicate on the diagram the:
   - polarity of each electrode
   - direction of electron flow
   - direction of negative ion flow
   - the EMF reading of the voltmeter
   - the anode
   - the cathode

b) Write the balanced half equations for the reactions occurring at the:
   - anode \( \text{Cd(s)} \rightleftharpoons \text{Cd}^{2+}(aq) + 2\text{e}^- \)
   - cathode \( \text{Ni}^{2+}(aq) + 2\text{e}^- \rightleftharpoons \text{Ni(s)} \)

c) The cell is recharged by connecting the terminals to a power source. Indicate on the diagram the:
   - polarity of each electrode
   - direction of electron flow
   - direction of negative ion flow
   - the anode
   - the cathode

e) Write the balanced half equations for the reactions occurring at the:
   - anode \( \text{Ni(s)} \rightleftharpoons \text{Ni}^{2+}(aq) + 2\text{e}^- \)
   - cathode \( \text{Cd}^{2+}(aq) + 2\text{e}^- \rightleftharpoons \text{Cd(s)} \)

f) Which of the following voltages should be used to recharge the cell shown above? Explain

0.15 V, 0.10 V, 0.20 V.

A voltage greater than the discharge voltage (0.15 V) needs to be used. Hence 0.20 V is necessary.