5 Climate change has forced manufacturers to look at alternative ways to store and generate electricity instead of using non-renewable fossil fuels. Batteries operating on redox principles have generated much traction and popularity.

Currently, lithium-ion batteries are used commercially in portable batteries and electric vehicles. They are the most ubiquitous batteries found in the market.

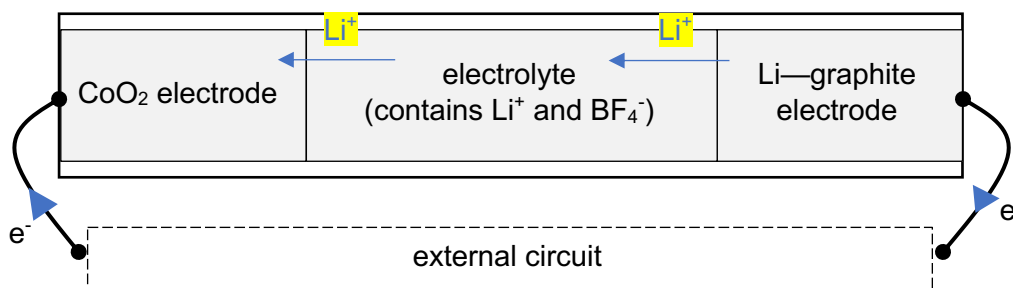**(a)** Fig 5.1 is a diagram representing a simplified lithium-ion battery.

Fig 5.1

Lithium atoms are stored in graphite. During the discharge process, the Li—graphite electrode is the anode, while the CoO_2 electrode is the cathode. Li^+ ions migrate through the electrolyte to maintain charge balance.

The half equations, together with the standard reduction potentials, for the discharge process are shown in Table 5.1. The discharge process is spontaneous.

anode	$Li \rightarrow Li^+ + e^-$
cathode	$Li^+ + CoO_2 + e^- \rightarrow LiCoO_2$

Table 5.1

(i) On the diagram in Fig 5.1,
- indicate the direction of electron travel during the discharge process on the wires; and
- indicate the direction of Li^+ ion migration during the discharge process;

Answer indicated on Fig 5.1 [1]

A battery's *charge capacity* is measured in mAh.

A portable charger said to have a charge capacity 10000 mAh is able to discharge a constant current of 1 mA (milli-ampere) for a total of 10000 hours. The discharge of the lithium-ion portable charger stops when half of the amount of CoO_2 is converted to $LiCoO_2$.

In a lithium-ion portable charger of charge capacity 10000 mAh, half of its mass is made up of the chemicals comprising the electrodes only.

(ii) Calculate the amount of electrons that will flow through the wires for a full discharge of a fully charged portable charger.

$Q = It = 10000 \times 10^{-3} \times 60^2 = 36000$ C
$n(e^-) = Q/F = 36000/96500 = 0.37306 = 0.373$ mol
This is an application question assessing you on how you interpret mAh.

[2]

(iii) Find the **increase** in mass of the CoO_2 electrode after a full discharge of a fully charged portable charger.

Increase in mass is due to deposition of Li^+ ions into CoO_2. Hence, we find the mass of Li added to the electrode.
m(Li) = 6.9 × n(Li) = 6.9 × $n(e^-)$ = 6.9 × 0.37306 = 2.5741 g = 2.57 g
Remember to leave your final answer to 3 s.f.

[2]

(iv) The Li—graphite electrode contains 6 carbon atoms for every 1 lithium atom present when the portable charger is fully charged.

Given that the decrease in the mass of the Li—graphite electrode is 5% of the original weight of the Li—graphite electrode when the portable charger is fully charged, calculate the mass of the portable charger.

We work out the mass of each electrode when the portable charger is fully charged.
Mass of the Li—graphite electrode (when the portable charger is fully charged) = $\frac{2.5741}{0.05}$ = 51.482 g
$n(CoO_2)$ = 0.37306 × 2 = 0.74612 mol (The discharge of the lithium-ion portable charger stops when half of the amount of CoO_2 is converted to $LiCoO_2$.)
Mass of CoO_2 electrode (when the portable charger is fully charged)
= 0.74612(58.9 + 16.0 × 2) = 67.822 g

Total mass of portable charger = 2(51.482 + 67.822) = 238.61 g = 239 g

The electrodes only make up 50% of the mass of the portable charger.
(For comparison, a 10000 mAh rated portable charger is around 200 grams.)

[4]

(v) The charge density of a battery is defined as the charge capacity per unit mass of the battery.

Calculate the charge density of the portable charger in mAh g^{-1}.

Charge density = $\frac{10000}{238.61}$ = 41.9 mAh g^{-1}

[1]

(b) When the lithium-ion battery was developed in the 1970s, metallic lithium was used as one of the electrodes. However, those batteries were dangerous and often caught fires after cycles of discharging and recharging due to the formation of 'dendrites'.

(i) In commercial lithium-ion batteries, lithium ions are trapped between layers of graphene in graphite. Fig 5.2 illustrates how lithium ions (represented as Li) are packed in the Li—graphite electrode.

graphene layer

Li   Li   Li   Li   Li   Li

Li   Li   Li   Li   Li   Li
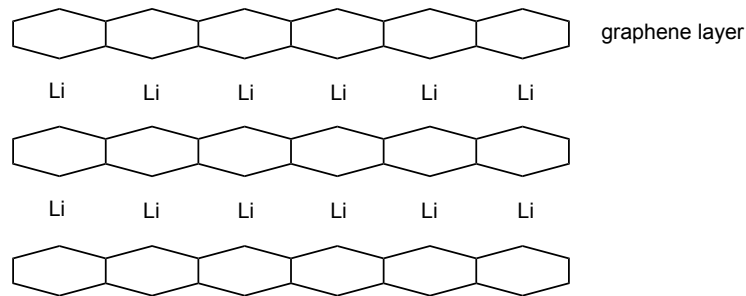
Fig 5.2

Compare the structure and bonding in the between the Li ions and graphene layers to that in metallic Li.

Metallic Li has a giant metallic lattice of Li^+ ions with a sea of delocalised electrons from the Li^+ ions. However, in the Li—graphite electrode, Li^+ ions are surrounded by a sea of delocalised electrons contributed from the graphene layers and Li.

There is electrostatic attraction between the sea of delocalised electrons and Li^+ ions, for both metallic Li and in the Li—graphite electrode.

....[2]

(ii) Cycles of discharging and recharging caused 'dendrites' of lithium to grow uncontrollably from the lithium electrode. Fig 5.3 illustrates such a phenomenon.

lithium electrode

dendrites of lithium
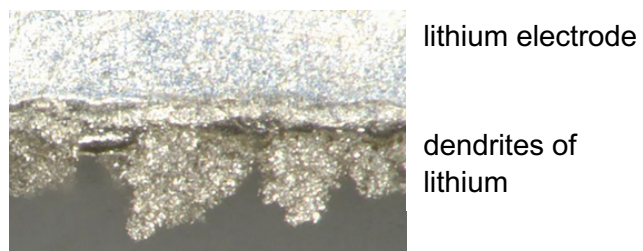
Fig 5.3

Eventually, these dendrites will grow and come into contact with the other electrode. Ignoring the danger this causes, suggest, with an explanation, what this does to the effectiveness of the battery.

When metallic Li touches the CoO_2 electrode, a spontaneous reduction of the CoO_2 to $LiCoO_2$ will occur. Electrons will travel through the Li dendrites to the CoO_2 electrode instead of the wires. This creates a short circuit, rendering the battery ineffective. (Take note that the short circuit is why the initial design of the Li-ion battery caught fire.)

[1]

(c) Sodium-ion batteries work with the same principles as the lithium-ion batteries. However, the materials of the electrode are different.

Table 5.2 lists some of the characteristics of a sodium-ion battery, compared to its cousin, the lithium-ion battery.

	Na-ion	Li-ion
common materials of electrodes	Fe, Mn, Ti, Cu	Co, Ni
energy density / Wh kg^{-1}	75 to 200	120 to 260
charge capacity per unit mass / mAh g^{-1}	150 to 200	300 to 360
cost per kWh of energy stored / USD kWh^{-1}	4 to 16	24 to 67
materials of electrolytes	polar aprotic organic solvents	

Table 5.2

(i) State a common property amongst the metals used to make the materials of the electrodes and hence suggest why these metals are used to make the electrodes.

They are transition metals / can exhibit multiple oxidation states.

They need to readily accept and lose electrons during charging and discharging.

... [2]

(ii) Suggest why the charge capacity of a Na-ion battery is typically lower than a Li-ion battery. Ignore any reference to materials used in the electrodes or electrolytes.

Both Na and Li can only lose one electron to form Na^+ or Li^+. However the atomic mass of Na is higher than that of Li. Hence, for the same mass of Na and Li, Na only loses less electrons than Li, resulting in a lower charge capacity for the Na-ion battery.

... [1]

(iii) A protic molecule is a molecule that has a hydrogen atom capable of being involved in hydrogen bonding. An aprotic solvent, however, lacks such hydrogen atoms.

Choose a suitable organic solvent from the organic molecules below that may be used in the electrolyte of both the Na-ion and Li-ion batteries. (Circle one)
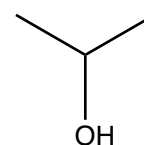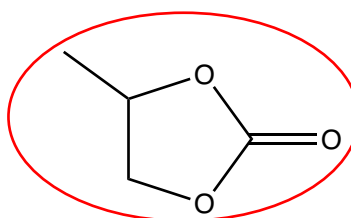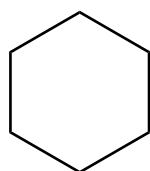
[1]

(iv) Suggest why the solvent must be polar and aprotic.

- Polar solvents promote the formation of favourable ion-dipole interactions between the solvent molecule and the ions in the electrolyte. This ensures that the Li^+/Na^+ ions are mobile and can act as mobile charge carriers and be present at the metal oxide electrode for reduction to take place.
- Protic solvents (especially those with –OH functionalities) may react with Li or Na atoms in a redox process, irreversibly oxidising them to Li^+/Na^+ ($2\ RH + 2\ Na \rightarrow H_2 + 2\ Na^+ + 2R^-$). H_2 gas produced is flammable and will damage the battery. Hence, an aprotic solvent must be used. (This is why certain Li-ion batteries must be kept away from water. Li-ion batteries usually have a layer of waterproof coating to also prevent such an undesirable reaction from occurring.)

…
…
…
[2]

(v) Suggest a hazard of using organic solvents as the electrolytes.

They are **flammable**. When the battery overheats / catches a spark, the battery may catch a fire or even explode.

…

……………………………………………………………………………………………….[1]

(vi) Although the energy density and charge density of the Na-ion battery is generally lower than that of the Li-ion battery, the Na-ion battery is still preferred over the Li-ion battery in some energy storage systems.

By considering the materials used to make the batteries, suggest why Na-ion batteries are still preferred in some scenarios. Ignore any reference to cost.

Metals like Fe and Cu are easily found / common. Co and Ni are rarer and its mining is more destructive.
For example, cobalt is mined, sometimes with child labour, in the Democratic Republic of Congo. Now, Li-ion batteries are phasing in the use of Fe and phasing out the use of Co.

….
.[1]

(vii) Which battery (Na-ion or Li-ion) is more suitable for storing energy for the following systems?

- electric vehicles: Li-ion (due to its higher charge density)
- excess energy from a solar farm in a power grid: Na-ion (cheaper)

[1]

(d) Explain two advantages of using rechargeable batteries over fossil fuels to provide energy for our daily needs.

- Fossil fuels are limited and non-renewable, while rechargeable batteries can be charged by renewable sources (solar, wind etc.).
- Burning of fossil fuels emits a lot of greenhouse gases, contributes to global warming. While the materials of rechargeable batteries are non-renewable, their utility period is extended since batteries can undergo cycles of recharging after being used.
- Materials from rechargeable batteries are recyclable / can be salvaged when the battery is worn out, but fossil fuels take long to be reformed in the carbon cycle.
(These are possible answers.)

….
….
….
.[2]

[Total: 24]