MME2045 BLOCK F - Functional Materials

Functional materials find a wide range of important technical applications. In this Block we will cover a number of functional materials relevant to mechanical applications including energy materials for fuel cells, rechargeable batteries, supercapacitors; ferromagnetic materials; and piezoelectric materials.

This notes lists the key knowledge points you need to understand for **Energy Materials**.

Energy Materials

1. Rechargeable batteries

Two types of most commonly used rechargeable batteries are discussed here: lead-acid batteries and lithium ion batteries. The working principle of a lithium ion battery is demonstrated below.

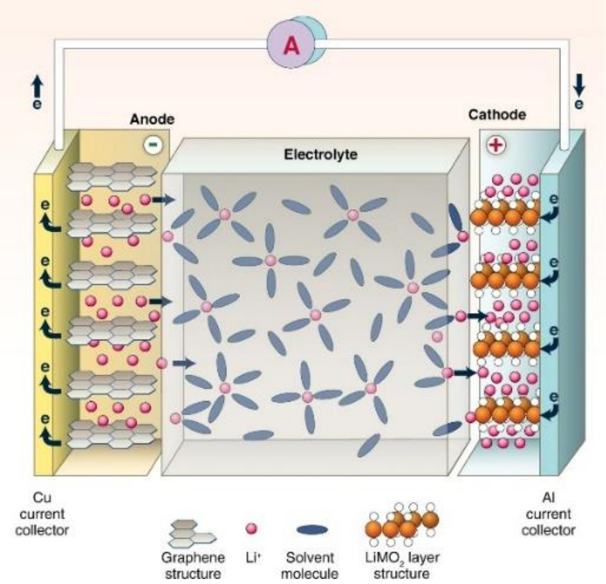

Figure 1. Schematic diagram of a lithium ion battery (Bruce Dunn, Haresh Kamath, Jean-Marie Tarascon, Science 2011, **334**, 928-935).

A rechargeable battery consists of three main components: anode, electrolyte and cathode (Figure 1) and generates electricity through an electrochemical reaction (Equation 1-3).

Anode (negative): $LiC_6(s) \rightarrow 6C(s) + Li^+ + e^-$ (1)

Cathode (positive): $FePO_4(s) + Li^+ + e^- \rightarrow LiFePO_4(s)$ (2)

Overall: $LiC_6(s) + FePO_4(s) \rightarrow 6C(s) + LiFePO_4(s)$ (3)

During charging, lithium ions are extracted from the cathode $LiFePO_4$, diffuse through the electrolyte, and are intercalated between the graphite sheets (the anode). The anode is the negative terminal as negatively charged electrons are produced here (Equation 1).

During discharge, Li ions return to the cathode via the electronically insulating electrolyte, and electrons pass around the external circuit. The electrolyte conduct Li ions only and does not conduct electrons.

The cell potential E is determined by the standard Gibbs free energy for the chemical reaction of the cell according to Equation 8:

$$\Delta G = -nFE \qquad (4)$$

F is the Faraday constant 96,485 C/mol

n is the number of electrons transferred per mole of reaction. n=1 for lithium ion battery and n=2 for lead acid battery.

Two key performance parameters for batteries:

Specific capacity: the amount of charge stored per unit mass. Common unit: mAh/g

Specific energy: the amount of electrical energy stored per unit mass. Common unit: Wh/kg

How to calculate theoretical specific capacity and density

Note that the commonly used units of capacity and energy for batteries are different from standard SI units.

$$1\text{ Ah} = 1\text{ Amp*hour} = 1\text{ C/s} * 3{,}600\text{s} = 3{,}600\text{ C} \qquad (5)$$

$$1\text{ Wh} = 1\text{ J/s} * 3{,}600\text{s} = 3{,}600\text{ J} \qquad (6)$$

$$\text{Specific capacity} = \frac{nF}{[3600\text{ C/Ah*MW}]} \qquad (7)$$

$$\text{Specific energy} = \frac{nFE}{[3600\text{ J/Wh*MW}]} \qquad (8)$$

Where F is the Faraday constant 96,485 C/mol

n is the number of electrons transferred per mole of reaction (n=1 for lithium ion battery and n=2 for lead acid battery).

E is cell potential.

MW is molecular weight of the active material to be considered.

For example, the molecular weight (MW) of the cathode material $LiFePO_4$ is 157.8 g/mol. The cell potential (E) is 3.3 V.

$$\text{Specific capacity} = \frac{1\times96485\text{C/mol}}{[3600\ \text{C/Ah}\times157.8\text{g/mol}]} = 0.170\ \text{Ah/g} = 170\ \text{mAh/g}$$

$$\text{Specific energy} = \frac{1\times96485\text{C/mol}\times3.3\text{V}}{[3600\ \text{J/Wh}\times157.8\text{g/mol}]} = 0.560\ \text{Wh/g} = 560\ \text{Wh/kg}$$

The practical specific capacity and enery are lower than the above theoretic values. For example, the practical specific energy for the state-of-the-art lithium ion batteries is about **200-250 Wh/kg**.

How to calculate practical specific energy of a battery

Figure 2. A commercial lead-acid battery.

Figure 2 shows that a commercial lead-acid battery has a nominal capacity of 41 Ah and voltage of 12 V. It weighs 11.8 kg.

The maximum energy stored in the battery is 41 Ah ×12 V = 492 Wh/kg

Noe that the unit is already in Wh. Conversion between J and Wh is not needed here.

The specific energy = 492 Wh / 11.8 kg = **41.7 Wh/kg**

Note that the theoretical specific density for a lead-acid battery is 171 Wh/kg.

The low practical specific energy compared to theoretical specific energy is due to low utilisation efficiency of the active mass (electrolyte and electrode materials) and the mass of peripheral materials (e.g., grid metal, separators, connectors, terminals, cell container).

Understand the meaning of the terms below.

Specific Energy (Wh/kg) – The nominal battery **energy per unit mass**, sometimes referred to as the gravimetric energy density.

Specific Power (W/kg) – The maximum available **power per unit mass**.

Energy Density (Wh/L) – The nominal battery **energy per unit volume**, sometimes referred to as the volumetric energy density.

Power Density (W/L) – The maximum available **power per unit volume**.

Understand the different types of lithium ion batteries defined by the physical size.

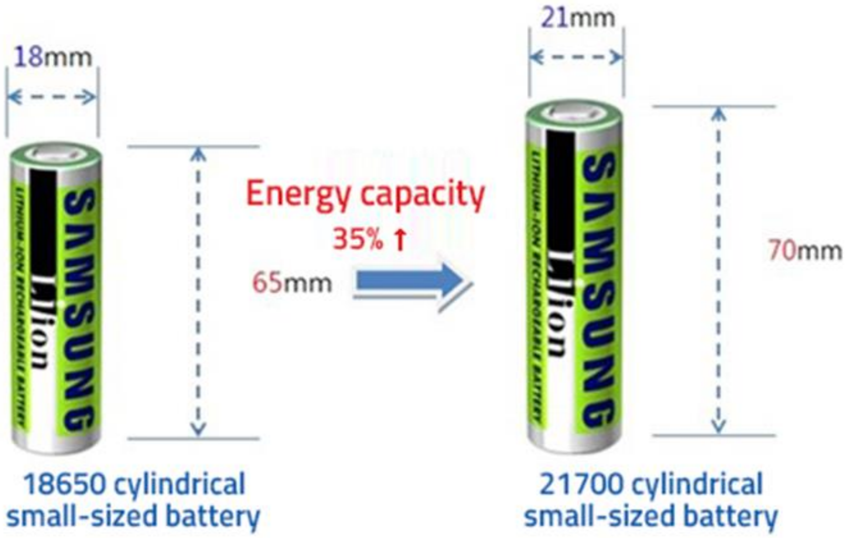

Figure 3. The 18650 and 21700 cylindrical type lithium ion battery.

The 18650 battery is 18mm in diameter, 65mm in length, the 0 for cylinder shape.

The 21700 battery is 21mm in diameter, 70mm long, the 0 for cylinder shape.

2. Fuel cells

Fuel cells can convert chemical fuels directly into electricity by an electrochemical reaction and offer high energy conversion efficiency, low CO_2 emission and pollution. The working principle of fuel cells can be demonstrated using a proton exchange membrane fuel cell (PEMFC), Figure 4.

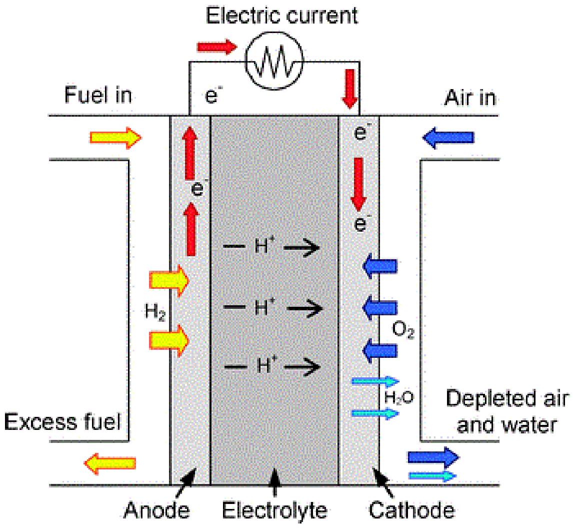

Figure 4. Schematic diagram of a proton exchange membrane fuel cell (Chem. Soc. Rev., 39 4370, 2010).

A PEMFC consists of mainly three key components: **anode, electrolyte and cathode**.

The anode and cathode are made of porous carbon coated with tiny particles of platinum. The function of the anode is to split molecular hydrogen (H_2) into protons and electrons, Equation 9.

The electrons travel to the cathode side of the cell through an external circuit (supplying power). The protons travel through the electrolyte to the cathode side where molecular oxygen (O_2) reacts with protons and electrons to produce water, Equation 10.

The electrolyte is made of proton-exchange membrane which conducts protons but not electrons (otherwise electrons could travel to the cathode through the membrane and cause ‘short circuits’ of the cell).

The overall cell reaction is given in Equation 11. PEMFCs are typically operated at 80 °C.

Anode (negative): $H_2 \rightarrow 2H^+ + 2e^-$ (9)

Cathode (positive): $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (10)

Overall reaction: $H_2 + 1/2O_2 \rightarrow H_2O$ (11)

The thermodynamic efficiency of a fuel cell is given by the ratio of the change of Gibbs free energy (ΔG, Equation 12) to the change of enthalpy (ΔH, Equation 12) associated with the overall cell reaction.

$$\Delta G = \Delta H - T\,\Delta S \qquad (12)$$

Where G is Gibbs free energy, H is enthalpy, S is entropy. ΔG is the maximum energy that can be used to do useful work whereas ΔH is the total energy (heat) involved in the whole cell reaction.

For the total cell reaction (Equation 11), ΔH is – 285.83 kJ/mol and ΔG is – 237.13 kJ/mol at 25 °C under standard pressure (1 atm) for H_2 and O_2 (water is in liquid form).

The theoretical efficiency of the cell is $\eta = \Delta G / \Delta H = (-237.13\ \text{kJ/mol}) / (-285.83\ \text{kJ/mol}) = 83\%$.

Practical efficiency for PEMFCs is typically in the range of 50-60%. The lower practical efficiency is mainly caused by incomplete utilisation of fuels and cell internal resistance associated with electrolyte and anode/cathode.

A fuel cell is different from a rechargeable battery in that, once the electricity stored in a battery is used up, the battery needs to be recharged. A fuel cell requires external supply of fuels to generate electricity. As long as fuels from external sources are provided, it can run indefinitely (in theory).

3. Supercapacitors

Most supercapacitors are double-layer capacitors (EDLCs) made of highly porous carbon electrodes kept apart by a separator, Figure 5. Electrostatic charge is stored at the thin interfaces (typically 1-10 nm) between the electrolyte and electrodes.

No chemical reactions are involved, which gives fast charge/discharge rates. Note that for both fuel cells and batteries, chemical reactions are required to generate/store energy.

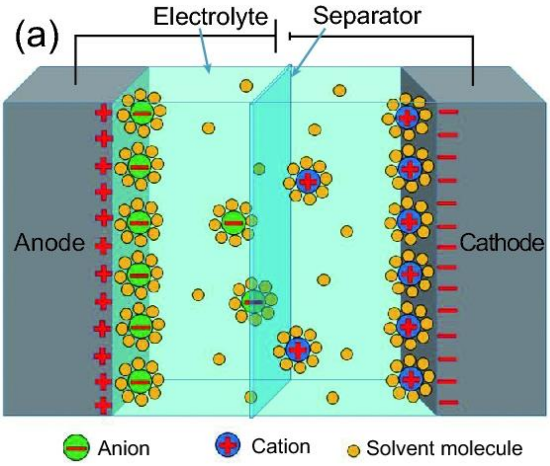

Figure 5. Schematic representation of an electrical double-layer capacitor (EDLC). National Science Review, 2017, 4, Pages 453–489.

The energy stored in a supercapacitor is given by Equation 13:

$$E = CU^2/2 \qquad (13)$$

Where, E is energy, C is capacitance (F), U is voltage (V).

The specific energy of supercapacitors is low (typically **1-10 Wh/kg**) compared to that of batteries. For example, a commercial supercapacitor has a rated voltage: 3.0 V, capacitance: 5000 F and mass: 2,000 g.

$$E = 5000F \times 3.0V^2/2 = 22.5kJ$$

Converting the energy unit from J to Wh:

22.5 kJ / 3600 Wh/J = 6.25 Wh

The specific energy is 6.25Wh / 2kg = 3.125 Wh.kg.

Key points:

- Working principle of batteries, fuel cells and supercapacitors
- Be able to distinguish between anode, cathode, negative electrode and positive electrode
- How to calculate the specific capacity and specific energy for batteries
- How to calculate the specific energy for supercapacitors
- Ballpark figures of specific energy of lead-acid, lithium-ion batteries and supercapacitors
- The advantages and disadvantages of lead-acid and lithium-ion batteries, fuel cells and supercapacitors