Dr. Norbert Cheung's Series in Electrical Engineering

Level 5 Topic no: 24

Energy Source

Contents

- 1. Energy and Battery Capacity
- 2. Lead Acid Batteries
- 3. Nickel Based Batteries
- 4. Metal Air Batteries
- 5. Sodium Batteries
- 6. Lithium Batteries
- 7. Battery Technologies Comparison
- 8. Fuel Cells
- 9. Ultra Capacitors
- 10. Flywheels

Reference:

C.C. Chan and K.T. Chau, Modern Electric Vehicle Technology, London: Oxford, University Press, 2001

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1. Battery and Energy Capacity

The mission of all EV energy sources is to supply electrical energy for propulsion. Thus, the energy capacity EC of these sources is usually represented by using the unit in Wh, which is defined by:

$$
EC = \int_0^t v(t)i(t)dt,
$$

where $v(t)$ is the instantaneous source voltage in V, $i(t)$ is the instantaneous discharging current in A, and t is the discharging period in h. If $v(t)$ is not considered, it will be termed as the coulometric capacity CC in Ah as defined by:

$$
CC = \int_0^t i(t)dt.
$$

The theoretical energy capacity in Wh can well represent the energy content of most EV energy sources except the electrochemical batteries. The reason is simply because batteries cannot be discharged down to zero voltage; otherwise, they may be permanently damaged. So, as shown in Fig. 6.1, a cut-off voltage needs to be defined at the 'knee' of the discharging curve of a particular battery at which a battery is considered to be fully discharged, so-called 100% depth-of-discharge (DOD). Thus, the energy capacity and coulometric capacity of batteries available before reaching the cut-off voltage are termed as the usable energy capacity

Discharging current

Fig. 6.1. Cut-off voltage of batteries.

For batteries, the usable coulometric capacity and hence usable energy capacity generally vary with their discharging current, operating temperature and ageing. The discharging/charging current is usually expressed by the discharging/charging rate:

$$
I = kC_n,
$$

where I is the discharging/charging current, n represents the C rate at which the battery coulometric capacity was rated, C is the rated coulometric capacity, and k is a multiple or fraction of C. For examples, the $C/5$ rate for a battery rated at 5 Ah denotes that the discharging current is of $kC_n = (1/5) \times 5 = 1$ A; a 10 Ah battery is discharged at 2 A can be denoted by the rate of $I/C_n = (2/10)C = 0.2 C$ or C/5. Thus, the usable energy capacity or coulometric capacity of batteries should be quoted together with the value of C rate, and they generally decrease with increasing the C rate.

Other useful indicators:

- Depth of Discharge (DOD) 100% when reach the cut-off knee point
- State of Charge (SOC) Ratio of present capacity over fully charge capacity
- Energy Density expressed as Watt-Hour per Litre
- Power Density deliverable energy per unit volume or mass (W/l or W/kg)
- Life Cycle usually quoted as 400 at 100% DOD; 1000 at 70% DOD, etc.

The basic element of each battery is the electrochemical cell. A connection of a number of cells in series forms a battery. Figure 6.2 shows the basic principle of the electrochemical cell or batteries in which both the positive electrode (P) and

FIGURE 3.1 Components of a battery cell. (a) Cell circuit symbol; (b) cell cross-section.

negative electrode (N) are immersed in the electrolyte (E). During discharge, the negative electrode performs oxidation reaction which drives electrons to the external circuit, while the positive electrode carries out reduction reaction which accepts electrons from the external circuit. During charge, the process is reversed so that electrons are injected into the negative electrode to perform reduction while the positive electrode releases electrons to carry out oxidation.

Performance goals	Mid-term	Long-term
Primary		
Specific energy $(C/3)$ discharge rate) (Wh/kg)	80 (100 desired)	200
Energy density $(C/3)$ discharge rate) (Wh/l)	135	300
Specific power (80% DOD/30s) (W/kg)	150 (200 desired)	400
Power density (W/l)	250	600
Life (years)	5	10
Cycle life (80% DOD) (cycles)	600	1000
Ultimate price (US\$/kWh)	< 150	< 100
Operating temperature $(^{\circ}C)$	$-30 - 65$	$-40 - 85$
Recharge time (h)	≤ 6	3 to 6
Fast recharge time (40–80% SOC) (h)	0.25	
Secondary		
Efficiency $(C/3)$ discharge, 6 h charge) $(\%)$	75	80
Self-discharge (%)	$<$ 15 (48 h)	\leq 15 (month)
Maintenance	no maintenance	
Abuse resistance	tolerance	
Thermal loss (for high-temperature batteries)	3.2 W/kWh	

Table 6.1 Performance goals of USABC

DOD: Depth-of-discharge SOC: State-of-charge

Nominal Energy Density of Sources

State of Charge Measurement

FIGURE 3.9 Battery SoC measurement.

 SoC measurement circuit is shown in Figure 3.9. The current is the rate of change of charge given by

$$
i(t) = \frac{dq}{dt}
$$

where q is the charge moving through the circuit. The instantaneous theoretical state of charge $SoC_T(t)$ is the amount of equivalent positive charge on the positive electrode. If the state of charge is Q_T at the initial time t_o , then $SOC_T(t_o) = Q_T$. For a time interval dt ,

$$
dSoC_T = -dq
$$

$$
= -i(t)dt
$$

Integrating from the initial time t_o to the final time t , the expression for instantaneous state of charge is obtained as follows:

$$
SoC_T(t) = Q_T - \int_o^t i(\tau) d\tau
$$
\n(3.2)

3.5.3 RAGONE PLOTS

In lead-acid and other batteries, there is a decrease in charge capacity (excluding voltage effects) with increasing currents. This is often referred to as the Ragone relationship and is described by Ragone plots. Ragone plots are usually obtained from constant power discharge tests or constant current discharge plots. Consider the experiment of Figure 3.13, but this time, the current i is adjusted by varying R_L

FIGURE 3.17 Specific power vs. specific energy (Ragone plots) of batteries, gasoline engine, and fuel cell.

$2.$ **Lead Acid Batteries**

The Pb-Acid battery has the nominal cell voltage of 2V, specific energy of 35 Wh/kg, energy density of 70 Wh/l, and specific density of 200 W/kg. It uses metallic lead as the negative electrode and lead dioxide as the positive electrode. The electrolyte is a sulphuric acid solution. The overall electrochemical reactions are:

 $Pb + PbO₂ + 2H₂SO₄ \leftrightarrow 2PbSO₄ + 2H₂O.$

The nominal voltage of the Pb-Acid cell is 2V. On discharge, the cutoff voltage at moderate rates is $1.75V$ and may be as low as $1.0V$ at extremely high rates at low temperatures. On charge, the charging current should be controlled to maintain the cell voltage lower than the gassing voltage (about 2.4 V). Otherwise, the overcharge reactions begin, resulting in the production of hydrogen and oxygen gases with the loss of water:

$$
2H_2O \rightarrow 2H_2 + O_2.
$$

- Relatively low cost
- Easy availability of raw materials (lead, sulfur)
- Ease of manufacture
- Favorable electromechanical characteristics

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Lead-acid battery: cell discharge operation.

Lead-acid battery: cell charge operation.

3. Nickel Based Batteries

Nickel Cadmium (Ni-Cd) Battery

The Ni-Cd battery possesses the nominal parameters of 1.2V, 56 Wh/kg, 110 Wh/l and 225 W/kg. Its active materials are metallic cadmium for the negative electrode and nickel oxyhydroxide for the positive electrode. The alkaline electrolyte is an aqueous potassium hydroxide solution. The electrochemical reactions of discharge and charge are:

$$
Cd + 2NiOOH + 2H2O \leftrightarrow Cd(OH)2 + 2Ni(OH)2.
$$

The Ni-Cd battery technology has gained enormous technical importance because of the advantages of high specific power (over $220 W/kg$), long cycle life (up to 2000 cycles), highly tolerant of electrical and mechanical abuse, flat voltage profile over a wide range of discharge currents, rapid recharge capability (about 40–80% in 18 min), wide operating temperature range $(-40-85\degree C)$, low self-discharge rate $(<0.5\%$ per day), excellent long-term storage

Nickel Zinc (Ni-Zn) Battery

The Ni-Zn battery nominally operates at 1.6 V and delivers 60 Wh/kg, 120 Wh/l and 300 W/kg. It uses zinc as the negative electrode and nickel oxyhydroxide as the positive electrode. The electrolyte is an alkaline potassium hydroxide solution. The discharge and charge reactions are:

$$
Zn + 2NiOOH + 2H2O \leftrightarrow Zn(OH)2 + 2Ni(OH)2.
$$

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Compared with conventional and other nickel-based batteries, the Ni-Zn battery has the advantages of higher specific energy and specific power than the Ni-Cd (60 Wh/kg and 300 W/kg), high cell voltage (highest of the nickel-based family), lower projected cost than the Ni-Cd (100-300 US\$/kWh), non-toxicity (more environmental friendliness than the Ni-Cd), tolerance of overcharge and overdischarge, capable of high discharge and recharge rates, and wide operating temperature range $(-20-60 \degree C)$. However, the major and serious drawback of the Ni-Zn battery is its short cycle life (about 300 cycles).

Nickel Metal-Hydride (Ni-MH) Battery

Since the Ni-MH battery is still under continual development, its advantages based on present technology are summarized as: highest specific energy and energy density of nickel-based batteries (65 Wh/kg and 150 Wh/l), environmental friendliness (cadmium free), flat discharge profile (similar to Ni-Cd), and rapid recharge capability (similar to Ni-Cd). However, it still suffers from the problem of high initial cost. Also, it may have a memory effect and be exothermic on ge.

lyte. The overall electrochemical reactions are:

 $MH + NiOOH \leftrightarrow M + Ni(OH)_{2}.$

4. Metal Air Batteries

The general advantages of rechargeable metal/air batteries, including the electrically or mechanically rechargeable zinc/air (Zn/Air), and mechanically rechargeable aluminium/air (Al/Air), are very high specific energy and energy density (as high as 600 Wh/kg and 400 Wh/l for Al/Air), low cost (only common metal and ambient air), environmental friendliness, flat discharge voltage, and capacity independent of load and temperatures. In addition, those mechanically rechargeable batteries have two distinct advantages which are very essential for EV applications: fast and convenient refuelling (comparable to petrol refuelling with a few minutes), and centralized recharging/recycling (most efficient and environmentally sound use of electricity). On the other hand, there are some general disadvantages associated with rechargeable metal/air batteries. They are with low specific power (at most 105 W/kg for Zn/Air), relatively limited temperature range, carbonation of alkali electrolyte due to carbon dioxide in air, and evolution of hydrogen gas from corrosion in electrolyte.

Zinc Air Battery:

$$
2Zn + O_2 \leftrightarrow 2ZnO.
$$

Can be recharged electrically or mechanically

The mechanically rechargeable Zn/Air battery can avoid the need for a bidirectional air electrode and the shape change problems of the zinc electrode resulting from charge-discharge cycling. Hence, it can offer higher specific energy and specific power, namely 230 Wh/kg and 105 W/kg. The mechanically refuelling system being considered for EV applications is to remove and replace the depleted zinc negative electrode cassettes robotically at a fleet servicing location or at a public service station. The discharged fuel is then electrochemically recharged at central facilities that serve regional distribution networks.

Aluminum Air Battery:

$$
4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al}(\text{OH})_3.
$$

The Al/Air battery with a saline electrolyte is attractive only for low power applications. On the other hand, the alkaline Al/Air battery can offer high specific energy and energy density of 250 Wh/kg and 200 Wh/l and is suitable for high power applications. Nevertheless, the corresponding specific power is as low as $7 W/kg$.

5. Sodium Batteries

Sodium Sulpher Battery

The Na/S battery operates at 300–350 °C with the nominal cell voltage of 2V, specific energy of 170 Wh/kg, energy density of 250 Wh/l and specific power of 390 W/kg.

$$
2Na + xS \leftrightarrow Na_2S_x \quad (x = 5-2.7).
$$

Sodium Nickel Chloride Battery

$$
2Na + NiCl_2 \leftrightarrow Ni + 2NaCl.
$$

Na/NiCl₂ battery still

has the disadvantages of potentially higher cost (relatively high cost of nickel), and lower specific power (150 W/kg for the $Na/NiCl₂$ and 200 W/kg for the Na/S).

6. Lithium Batteries

Li-Polymer battery

The Li-Polymer battery uses lithium metal and a transition metal intercalation oxide (M_vO_z) for the negative and positive electrodes, respectively. This M_vO_z possesses a layered structure into which lithium ions can be inserted or from where they can be removed on discharge and charge, respectively. A thin solid polymer electrolyte (SPE) is used, which offers the merits of improved safety and flexibility in design. The general electrochemical reactions are:

$$
xLi + M_yO_z \leftrightarrow Li_xM_yO_z.
$$

It operates at the nominal voltage of 3 V and has the specific energy of 155 Wh/kg, energy density of 220 Wh/l and specific power of 315 W/kg. The corresponding advantages are high cell voltage $(3 V)$, very high specific energy and energy density (155 Wh/kg and 220 Wh/l), very low selfdischarge rate (about 0.5% per month), capability of fabrication in a variety of shapes and sizes, and safer design (reduced activity of lithium with solid electrolyte). However, it has a drawback of relatively weak low-temperature performance due to its temperature dependence of ionic conductivity.

Li-Ion battery

Since the first announcement of the Li-Ion battery in 1991, the Li-Ion battery technology has seen an unprecedented rise to what is now considered to be the most promising rechargeable battery of the future. Although still in the stage of development, the Li-Ion battery has already gained acceptance for EV applications.

The general electrochemical reactions are described as:

$$
Li_xC + Li_{1-x}M_yO_z \leftrightarrow C + LiM_yO_z.
$$

On discharge, lithium ions are released from the negative electrode, migrate via the electrolyte and are taken up by the positive electrode. On charge, the process is reversed. Possible positive electrode materials include $Li_{1-x}CoO_2$, $Li_{1-x}NiO_2$ and $Li_{1-x}Mn_2O_4$, which have the advantages of stability in air, high voltage and reversibility for the lithium intercalation reaction.

The general advantages of the Li-Ion battery are highest cell voltage (as high as 4V), high specific energy and energy density (90–130 Wh/kg and 140–200 Wh/l), safest design of lithium batteries (absence of metallic lithium), and long cycle life (about 1000 cycles). However, it still suffers from a drawback of relatively high self-discharge rate (as high as 10% per month).

7. Battery Techonologies Comparison

Table 6.2 Key parameters of EV batteries

NA: Not available $^{\rm a}$ At C/3 rate b At 80% DOD ^cMechanical recharging ^dFor reference only

8. Fuel Cells

The key advantage of fuel cells over batteries is that a fuel cell powered EV can give a driving range comparable to an ICEV because its range is determined only by the amount of fuel available in the fuel tank, and is independent of the size of fuel cells. Actually, the size of fuel cells is only governed by the required power level of EVs. Other major advantages of fuel cells are that their reactant feeding time is generally much shorter than the recharging time of batteries (except for those mechanically rechargeable ones), their lifetime is generally much longer than that of batteries, and they generally require less maintenance than batteries.

Table 6.4 Theoretical energy contents of prominent fuels

^aAt ambient temperature and 20 MPa

^bAt cryogenic temperature and 0.1 MPa

TABLE 4.1 Fuel Cell Types

4.1.2 FUEL CELL TYPES

The six major types of fuel cells are as follows: alkaline, proton exchange membrane, direct methanol, phosphoric acid, molten carbonate, and solid oxide. A short description of the relevant characteristics of each type in the context of vehicular and stationary applications is given below.^{2,3}

4.1.2.1 Alkaline Fuel Cell (AFC)

In an alkaline fuel cell (AFC), an aqueous solution of potassium hydroxide (KOH) is used as the electrolyte. Compared to some other fuel cells where acidic electrolytes are used, the performance of the alkaline electrolyte is as good as the acid electrolytes, while being significantly less corrosive toward the electrodes. Alkaline fuel cells have been in actual use for a long time, delivering electrical efficiencies of up to 60%. They require pure hydrogen as fuel and operate at low temperatures (at 80°C); therefore, they are suitable for vehicle applications. Residual heat can be used for heating, but the cell temperature is not sufficiently high to generate steam that can be used for cogeneration.

4.1.2.2 Proton Exchange Membrane (PEM)

The proton exchange membrane (PEM) fuel cells use solid electrolytes and operate at low temperatures (around 80° C). Nafion is an example of solid polymer electrolyte. These fuel cells are also known as solid polymer membrane fuel cells. The electrical efficiency of PEM fuel cells is lower than that of the alkaline cells (about 40%). However, a rugged and simple construction makes these types of fuel cells suitable for vehicle applications. The PEM fuel cell and the AFC are currently being considered for vehicle applications. The advantage of PEM cells is that they can tolerate impurity in the fuel, as compared to pure hydrogen which is needed in alkaline fuel cells.

4.1.2.3 Direct Methanol Fuel Cell (DMFC)

The direct methanol fuel cell (DMFC) is a result of research on using methanol as the fuel that can be carried on-board a vehicle and reformed to supply hydrogen to the fuel cell. A DMFC works on the same principle as the PEM, except that the temperature is increased to the range of 90 to 120° C such that internal reformation of methanol into hydrogen is possible. The electrical efficiency of DMFC is quite low at about 30%. This type of fuel cell is still in the design stages, because the search for a good electrocatalyst to reform the methanol efficiently and to reduce oxygen in the presence of methanol is ongoing.

4.1.2.4 Phosphoric Acid Fuel Cell (PAFC)

Phosphoric acid fuel cells (PAFC) are the oldest type with an origin that extends back to the creation of the fuel cell concept. The electrolyte used is phosphoric acid, and the cell operating temperature is about 200^oC, which makes some cogeneration

possible. The electrical efficiency of this cell is reasonable at about 40%. These types of fuel cells are considered too bulky for transportation applications, while higher efficiency designs exist for stationary applications.

Molten Carbonate Fuel Cell (MCFC) $4.1.2.5$

Molten carbonate fuel cells, originally developed to operate directly from coal, operate at 600° C and require CO or CO₂ on the cathode side and hydrogen on the anode. The cells use carbonate as the electrolyte. The electrical efficiency of these fuel cells is high at about 50%, but the excess heat can be used for cogeneration for improved efficiency. The high temperatures required make these fuel cells not particularly suitable for vehicular applications, but they can be used for stationary power generation.

4.1.2.6 Solid Oxide Fuel Cell (SOFC, ITSOFC)

Solid oxide fuel cells (SOFCs) use a solid ionic conductor as the electrolyte rather than a solution or a polymer, which reduces corrosion problems. However, to achieve adequate ionic conductivity in such a ceramic, the system must operate at very high temperatures. The original designs, using yttria-stabilized zirconia as the electrolyte, required temperatures as high as 1000° C to operate, but the search for materials capable of serving as the electrolyte at lower temperatures resulted in the "intermediate temperature solid oxide fuel cell" (ITSOFC). This fuel cell has high electrical efficiency of 50 to 60%, and residual heat can also be used for cogeneration. Although not a good choice for vehicle applications, it is at present the best option for stationary power generation.

FIGURE 4.3 Fuel-cell-based EV.

9. Ultra Capacitors

Because of frequent start/stop operation of EVs, the discharge profile of the battery is highly variable. The average power required from the battery is relatively low while the peak power of relatively short duration required for acceleration or hill climbing is much higher. Th

In the foreseeable development of the ultracapacitor, it cannot be used as a sole energy source for EVs because of its exceptionally low specific energy. Neverthe less, there are a number of advantages that can be resulted from using the ultracapacitor as an auxiliary energy source. The promising application is the so-called battery & ultracapacitor hybrid energy system for EVs. Hence, the specific energy and specific power requirements of the EV battery can be decoupled, thus affording an opportunity to design the battery that is optimized for the specific energy and cycle life with little attention being paid to the specific power. Due to the load levelling effect of the ultracapacitor, the high-current discharge from the battery is minimized so that the available energy, endurance and life of the battery can be significantly increased. Moreover, compared to the battery, the ultracapacitor can provide much faster and more efficient energy recovery during regenerative braking of EVs.

The double-layer capacitor technology is the major approach to achieve the ultracapacitor concept. The basic principle of a double-layer capacitor is illustrated in Fig. 6.12. When a voltage is applied across the electrodes, a double layer is formed by the dipole orientation and alignment of electrolyte molecules over the entire surface of the electrodes. This polarization is used to store energy in the capacitor according to:

$$
C = \frac{\varepsilon A}{d}
$$

$$
E = \frac{1}{2}CV^2,
$$

where ε is the effective dielectric constant, d is the separation distance, A is the electrode surface area, C is the capacitance, V is the applied voltage and E is the stored energy. By adopting high-dielectric materials, short separation distances and large electrode surface areas, the capacitance can be greatly increased. At the present

Fig. 6.12. Basic principle of ultracapacitors.

The corresponding energy equation is given

$$
W_{\rm cap} = \left(\frac{1}{2}mv^2 + mgh\right)/\eta,
$$

where *m* is the total mass of the vehicle, *v* is the maximum vehicle speed, *g* is the gravitational acceleration, h is the maximum height difference of the vehicle mission and η is the system energy efficiency of the use of the ultracapacitor. Hence, the required capacitance C can be calculated by:

$$
W_{\rm cap} = \frac{1}{2} C (V_{\rm max}^2 - V_{\rm min}^2),
$$

where V_{max} and V_{min} are respectively the maximum and minimum voltage limits of the ultracapacitor.

10. Flywheels

The flywheel is the kind of energy supply unit that stores energy in mechanical form. Flywheels store kinetic energy within a rotating wheel-like rotor or disk made of composite materials. Flywheels have a long history of usage in automobiles, being routinely used in all of today's IC engines to store energy and smooth the power delivered by abrupt pulses of the engine. However, the amount of energy storage required in flywheels of IC engines is small and is limited by the need of the vehicle to accelerate rapidly. The flywheel is currently being looked into for use in a number of different capacities. Flywheels can be used in HEVs with a standard IC engine as a power assist device. Alternatively, flywheels can be used to replace chemical batteries in EVs to serve as the primary energy source or could be used in conjunction with batteries. However, technological breakthroughs in increasing the specific energy of flywheels are necessary before they can be considered as the energy source for EVs and HEVs. The flywheels of today are quite complex, large, and heavy. Safety is also a concern with flywheels.

The flywheel design objective is to maximize energy density. The energy U stored in the flywheel is given by

$$
U=\frac{1}{2}J\omega^2
$$

Flywheels have several advantages as an energy source, the most important of which is the high specific power. Theoretically, specific power of flywheels has been shown to be of the order of 5 to 10 kW/kg, with a specific power of 2 kW/kg being easily achievable without exceeding safe working stresses. Other performance features that make flywheels attractive can be attributed to their mechanical nature. Flywheels are not affected by temperature extremes. There are no concerns with toxic chemical processing and disposal of waste materials, making flywheels

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