

Chemical Storage

Chemical compounds containing hydrogen can also be considered as a kind of hydrogen storage. These include e.g. methanol CH_2OH , ammonia NH_3 , and methylcyclohexane $\text{CH}_3\text{C}_6\text{H}_{12}$. In STP condition all of these compounds are in liquid form. This is a clear advantage compared to gaseous hydrogen, which demands leak-proof, preferably seamless, piping and vessels. The hydrogen storage capacity of these chemical compounds is quite good – 8.9 wt% for CH_2OH , 15.1 wt% for NH_3 , and 13.2 wt% for $\text{CH}_3\text{C}_6\text{H}_{12}$. These figures do not include the containers in which the liquids are stored. Because the containers can be made of light-weighted composites or even plastic in some cases, the effect of a container is negligible especially with larger systems. Chemical storage of hydrogen has also **some disadvantages**. The storage method is non-reversible, i.e. the compounds cannot be “charged” with hydrogen reproducibly. The compounds must be produced in a centralized plant and the reaction products have to be recycled. This is difficult especially with ammonia, which produces highly pollutant and environmentally unfavorable nitrogen oxides. Other compounds produce carbon oxides, which are also quite unfavorable.

Batteries

Batteries are referred to as electrochemical or galvanic cells, due to the fact that they store electrical energy in the form of chemical energy and because the electrochemical reactions that take place are also termed galvanic. Galvanic reactions are thermodynamically favorable (the free energy difference, ΔG , is negative) and occur spontaneously when two materials of different positive standard reduction potentials are connected by an electronic load (meaning that a voltage is derived). The material with the lower positive standard reduction potential undergoes an oxidation reaction providing electrons by the external circuit to the material with the higher positive standard reduction potential, which in turn undergoes a reduction reaction. These half reactions occur

concurrently and allow for the conversion of chemical energy to electrical energy by means of electron transfer through the external circuit. It follows that the material with the lower positive standard reduction potential is called the negative electrode or anode on discharge (since it provides electrons), while the material with the higher positive standard reduction is called the positive electrode or cathode on discharge (since it accepts electrons). In addition to the electrodes, the two other constituents that are required for such reactions to take place are the electrolyte solution and the separator. The electrolyte is an ion conducting material, which can be in the form of an aqueous, molten, or solid solution, while the separator is a membrane that physically prevents a direct contact between the two electrodes and allows ions but not electrons to pass through; it therefore ensures electrical insulation for charge neutralization in both the anode and cathode once the reaction is completed. Two final parts required to complete a commercial galvanic cell are the terminals. They are necessary when applying the batteries to electrical appliances with specific holder designs in order to prevent short - circuit by battery reverse installation, and they are shaped so as to match the receptacle facilities provided in the appliances. For example, in cylindrical batteries, the negative terminal is either designed so as to be flat, or to protrude out of the battery end, while the positive terminal extends as a pip at the opposite end. A simple galvanic cell is illustrated in Figure 1.1 a, while Figure 1.1 b shows terminal designs for cylindrical batteries.

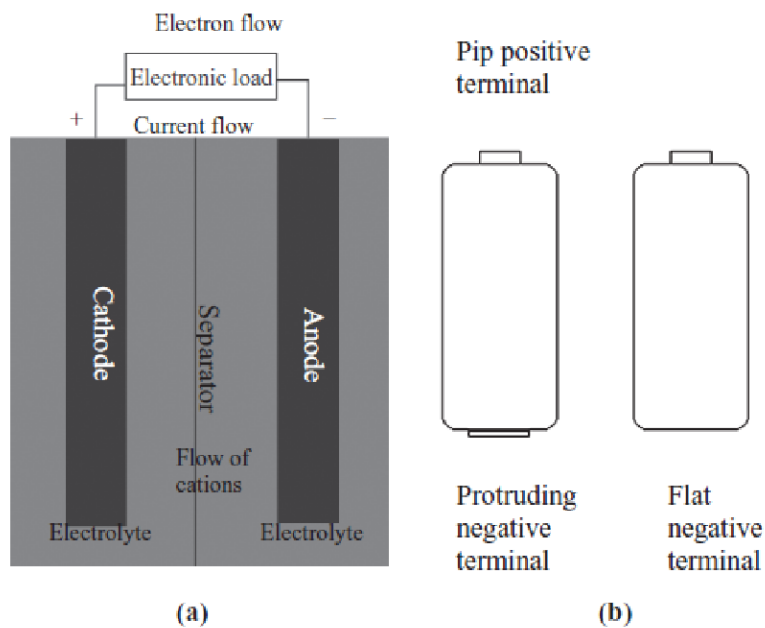


Figure 1.1 (a) The schematic diagram of a simple galvanic cell. (b) Terminal designs for cylindrical batteries.

Voltage

The theoretical standard cell voltage, E_0 (cell) can be determined using the electrochemical series and is given by the difference between the standard electrode potential at the cathode, E_0 (cathode), and the standard electrode potential at the anode, E_0 (anode) as

$$E_0 \text{ (cathode)} - E_0 \text{ (anode)} = E_0 \text{ (cell)}$$

The standard electrode potential, E_0 , for an electrode reaction, written (by convention) as a reduction reaction (i.e., involving consumption of electrons), is the potential generated by that reaction under the condition that the reactants and the products are in their standard state in relation to a reference electrode. In order to obtain a true estimate of the actual open circuit cell voltage in the fully charged state for operation of the battery, the theoretical cell voltage is modified by the Nernst equation, which takes into account the nonstandard state of the reacting component as

$$E = E_0 - RT \ln Q \quad (1.2)$$

Table 1.3 Battery characteristics [2].

Battery characteristics	Definition	Unit
Open-circuit voltage	Maximum voltage in the charged state at zero current	Volt (V)
Current	Low currents are characterized by activation losses, while the maximum current is normally determined by mass transfer limitations	Ampere (A)
Energy density	The energy that can be derived per unit volume of the weight of the cell	Watt-hours per liter (Wh/dm ³)
Specific energy density	The energy that can be derived per unit weight of the cell (or sometimes per unit weight of the active electrode material)	Watt-hours per kilogram (Wh/kg)
Power density	The power that can be derived per unit weight of the cell	Watt per kilogram (W/kg)
Capacity	The theoretical capacity of a battery is the quantity of electricity involved in the electrochemical reaction	Ampere-hours per gram (Ah/g).
Shelf-life	The time a battery can be stored inactive before its capacity falls to 80%	Years
Service life	The time a battery can be used at various loads and temperatures	Hours (usually normalized for ampere per kilogram (A/kg) and ampere per liter (A/l ³))
Cycle life	The number of discharge/charge cycles it can undergo before its capacity falls to 80%	Cycles

The Nernstian potential in Eq. (1.2) will change with time due to the self – discharge by which the activity (or concentration) of the electroactive component in the cell is modified. Thus, the nominal voltage is determined by the cell chemistry at any given point of time. The operating voltage produced is further modified as a result of discharge reactions actually taking place and will always be lower than the theoretical voltage due to polarization and the resistance losses (IR drop) of the battery as the voltage is dependent on the current, I , drawn by an external load and the cell resistance, R , in the path of the current. Polarization rises in order to overcome any activation energy for the electrode reaction and/or concentration gradients near the electrode. These factors are dependent upon electrode kinetics and, thus, vary with

temperature, state of charge, and with the age of the cell. Of course the actual voltage appearing at the terminal needs to be sufficient for the intended application.

Tafel Curves for a Battery

In a battery there are two sets of Tafel curves present, one for each electrode material. During discharge one material will act as the anode and the other as the cathode. During charging the roles will be reversed. The actual potential difference between the two electrodes for a given current density can be found from the Tafel curve. The total cell potential is the difference between the anodic potential, E_a , and the cathodic potential, E_c . In a galvanic cell, the actual potential, $V'_{cell, discharge}$, is less than the Nernst potential

$$V_{cell, discharge} = E_c - \eta_c + E_a - \eta_a \quad (1.28)$$

Upon discharge the cell potential may be further decreased by the ohmic drop due to the internal resistance of the cell, r . Thus, the actual cell potential is given by

$$V_{cell, discharge} = V_{cell, discharge} - iAr \quad (1.29)$$

where A is the geometric area relevant to the internal resistance and i is the cell

current density. Similarly, on charging the applied potential is greater than the Nernstian potential, and can be calculated by the equation

$$V_{cell, charge} = E_c + \eta_c + E_a + \eta_a \quad (1.30)$$

The cell charging potential may now be increased by the ohmic drop. The cell charging potential may now be increased by the ohmic drop, and the final actual cell charging potential is given by $V_{cell, charge} = V_{cell, charge} + iAr$ (1.31)

In summary, it can be stated that in order to maximize power density, it is important to achieve the most optimum value of cell potential at the

lowest overpotentials and internal resistance. Usually at low current densities, overpotential losses arise from an activation energy barrier related to electron transfer reactions, while at a higher current density, the transport of ions becomes rate limiting giving rise to a current limit. Ohmic losses increase with increasing current, and can be further enhanced by the increased formation of insulating phases during the progress of charging. Power is a product of voltage and current; therefore, decreasing the current density by increasing the true surface area can also in principle result in a higher power density. However, unwanted side reactions may also be enhanced.

Capacity

The bar graph of Figure 1.8 shows the difference between the theoretical and actual capacities in mAh g^{-1} for various battery systems. The theoretical molar capacity of a battery is the quantity of electricity involved in the electrochemical reaction. It is denoted as Q charge and is given by

$$Q \text{ charge} = xnF \quad (1.32)$$

where x is the number of moles of a chosen electroactive component that take place in the reaction, and n is the number of electrons transferred per mole of reaction. The mass of the electroactive component can be calculated as

$$M = xMr \quad (1.33)$$

where M denotes the mass of the electroactive component in the cell and Mr the molecular mass of the same component. The capacity is conventionally expressed as Ah kg^{-1} thus given in terms of mass, often called specific capacity, C specific

$$C \text{ specific} = nF/Mr \quad 1.34$$

If the specific capacity is multiplied by the mass of the electroactive component in the cell, one will obtain the rated capacity of a given cell. It is important to note that the mass may refer to the final battery mass including packaging or it may be reported with respect to the mass of the electroactive components alone. It is quite straightforward to recalculate the capacity in terms of the mass of the cell by dividing the rated capacity with the total mass of the cell.