Chapter 1
Basic Elements for Energy Storage and Conversion

1.1 Energy Storage Ability

One of the main challenges of the modern society is the so-called *energy transition for reducing the global warming* due to the great amount of exhausted carbon dioxide that will devastate our planet. The energy transition consists in replacing fossil fuels such as coal, gas, oil and to some extend nuclear energy by alternative renewable sources of energy that are solar radiation, wind, ocean, biomass, geothermal and hydro-electricity, which are less polluting. Moreover, this *green energy* is abundant except hydro-electricity which is limited by the number of available sites. Photovoltaic cells and wind mills are attracting due to the huge production of electricity coming from solar radiation conversion that is around one to two billion kWh, but they are intermittent sources and storage systems are required to satisfy the consumer demand at any time. Depending on the design of the system, the battery could supply energy for extended dark or cloudy or windless periods. Similar problem occurs with the capture of energy from ocean surface waves. Consequently, the main trend is the growing market not only for small-scale wind systems, but also for grid connected projects. From 1996 to 2009, the existing world capacity produced by wind power increased from 5 to 160 GW [1]. In February 2014, the installed wind energy capacity in the EU was 117.3 GW: 110.7 GW onshore and 6.6 GW offshore with the largest installed capacity (29 %) in Germany [2]. As society becomes increasingly more dependent on electricity, the development of systems capable of storing directly or indirectly this secondary energy form will be a crucial issue for the twenty-first century. As an example of the fast growth of electronics, six billion people out of the world's seven billion have access to mobile phones, equivalent to more than 85 % of global population [3].

The subject of energy storage is a major development in high technology, which bears considerable industrial potential. Batteries, which are devices converting the energy released by spontaneous chemical reactions to electricity work, have some extraordinary properties in these regards. They store and release electrical energy;

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they are portable and can be used flexibly with a short lead time in manufacture. Today, the high-tech mobile world including mobile phones, laptops, cameras depends on lithium-ion batteries with a quantity of five billion units sale in 2013 [4]. From the view point of energy consumption of portable electronics, operating currents vary from microamps to more than one ampere: cellular phone (200–800 mA), camcorder (700–1000 mA), notebook (500–1500 mA), video games (20–200 mA), remote control (10–60 mA), etc.

In this brief introduction, we provide a brief overview on energy storage systems from the conventional to the update systems before further going into the technology. Energy storage (ES) can be obtained through various ways depending on the stored energy:

- *Mechanical*, like water stored behind a dam (potential energy) or like high speed heavy wheel used to start marine engines (kinetic energy).
- *Electrical* in capacities (voltage is equivalent to potential energy) or in superconductive coils provided that high currents (equivalent to kinetic energy) can be used, which is not the case for high-Tc superconductors, while the limit for the others is the low temperature of the transition to the normal state.
- *Chemical* by storing separately two chemical elements like Li and F, or molecules like H_2SO_4 and H_2O able to react when in contact, producing a high value bonding energy. ES in explosives where the energy is obtained by chemical reorganization pertains to this class. In all these cases, the process uses some kind of stored potential energy, and differences in chemical potentials.
- *Electrochemical* storage is a variant of the chemical one where the stored energy depends on the difference of bonding energy between two different compounds of the same element, one used as anode, the other one as a cathode. Classical example is the lead-acid battery, where the oxidation degree of lead changes from one electrode to the other one. Now, a new very important component appears in the form of the electrolyte able to transport the ion that is $(SO_4)^{2-}$.

Note that in all the electrochemical systems, the flow of ions is always from anode to cathode for both charge and discharge process. In rechargeable batteries (as Li-ion cells), there is a confusing meaning when negative and positive electrodes are named anode and cathode either on charge or discharge. They are respectively the anode and cathode and reverse on charge to discharge and vice versa. Many battery engineers use this mistaken nomenclature for the electrodes as a historical artifact of primary (nonrechargeable) batteries which operate only in the discharge mode.

Two configurations exist for ES systems: In the first case, the chemical components are compressed together with a mechanical separator between the electrodes, and they are able to give only one discharge. Such systems are referred as primary batteries. In the other case of secondary batteries the system is reversible, as these cells can be recharged electrically, just as we do pump water at the top of a dam. A recent strategy is to use the high surface area of nano-structured active particles assembled in thin layers of charged species of high value capacities. The high surface area is also used to obtain super-capacitances. Several F g^{-1} are now easily produced with the constraints due to double-layer formation and potential stability (remain the earth capacity in space is ~1 F).

1.2 The Sustained Energy

It is well known that the present production on use of energy is responsible for serious problems to the global environment, particularly in relation to greenhouse gas emission such as carbon dioxide which provokes climate modification. The challenge in moving towards global energy sustainability can be assessed by the trends in the use of fuels for primary energy supplies. Table 1.1 gives statistics reported by the International Energy Agency (IEA) [5]. The total primary energy supply in the world, in megatons oil equivalent (Mtoe), was 5096 Mtoe in 1998. The IEA's forecast of the world demand is 13700 Mtoe in 2020.

The consequence of the big consumption of fossil energy is the global climate change. The *concentration of greenhouse gases (GHG)* in the atmosphere (including CO_2, CH_4, O_3, N_2O, and CFC) has increased very fast since the end of the nineteenth century. In 2011, the atmospheric concentration of CO_2 was 391 ppm against 278 ppm in 1750. Each year, 5 metric tons of carbon dioxide are added to the atmosphere for each person in the US but they are not included in the chart to ensure consistency with the other greenhouse gas figures [6].

Table 1.2 summarized the electricity production in TWh in the world in 2013. The total energy consumed at all power plants for the generation of electricity was approximately 4.4×10^6 ktoe (1 ktoe—kilo tonne of oil equivalent- is equal to 11630 MWh) [5]. The world's largest producer of electricity since 2011, China, has definitely outpaced the USA in 2012 with 4936.5 TWh against 4298.9 TWh. Chinese production increased by 11.5 % per year from 2002 to 2012, a tripling in 10 years. The thermal generation remains dominant, but renewable energy grew faster (12.5 % per year), increasing from 17.6 to 19.2 %. China is the world leader in the production of electricity from renewable sources with 949.2 TWh in 2012, far ahead of the USA (536.9 TWh) and Brazil (462.2 TWh).

Table 1.1 Total primary energy supply by fuel (in % terms) for the world and forecast (IEA data [5])

Energy supply	1973	1998	2010	2020
Oil	44.9	53.2	38.8	38.3
Coal, biomass, and waste	36.1	24.4	28.4	28.7
Gas	16.3	18.8	23.6	25.2
Nuclear	0.9	1.3	5.8	4.4
Hydroelectric power	1.8	2.1	2.6	2.6
Geothermal, wind, solar, and heat	0.1	0.2	0.7	0.8

Table 1.2 Electricity production in TWh in the world in 2013

Power source	Europe	North America	OCDE Asia Oceania	China[a]	India[b]
Fossil fuels	1661	3232	1462	3889	794
Nuclear	831	899	145	98	131
Hydroelectricity	601	724	135	823	29
Renewables	336	222	41	126	31
Total (TWh)	3429	5077	1783	4936	985

OCDE Asia includes Australia, Japan, Korea, and New Zealand
[a] Year 2012
[b] Year 2011

The goal of global energy sustainability implies the replacement of all fossil fuels (oil, coal, natural gas) by renewable energy sources (geothermal, biomass, hydrogen, batteries, etc.). The large explosion of systems capable to store energy may be considered to be due to influences related to economy and connected to basic problems in industrialized countries from the economical, environmental, technological, and political points of view. To meet the rapid development of energy storage devices, extensive researches are currently devoted to develop power sources, such as lithium-ion batteries (LiBs), supercapacitors (SCs), solar cells, and fuel cells. These devices require new technologies such as *nanotechnology* for light-weight and even implantable applications [7].

1.3 Energy Storage for Nano-electronics

The performance of devices reached today is the result of intensive research to reduce the size of the particles to the nanoscale. The use of nanotechnology has been increasing in modern electronics devices using CMOS semiconductors (Si or GaAs), which allow very high frequency. As an example, microprocessors today run at 1 GHz. It is important, however, to specify what "nano" means here. In electronics, for instance, it signifies particles that are so small the electronic or the magnetic properties are modified by quantum confinement of the electrons. It means particles smaller than 10 nm. In the physics and electrochemistry of the cathode elements of Li-ion batteries, the term is used to signify particles so small that their properties depend importantly on surface effects. Consider nano-grains of materials for batteries, typically, the surface layer of a grain is about 3 nm thick, so that particles are labelled "nano" in the literature if their size is smaller than 100 nm, and usually in the range 20–100 nm. More sophisticated assemblies combining for instance such particles with nano-forms of carbon such as graphene are encountered in the formation of negative electrodes in Chap. 10.

As the power consumption of a CMOS circuit, operating in a switching fashion, is proportional to the square of its supply voltage, such circuits should operate at the lowest possible supply voltage to extend the battery life. Meanwhile, electrical

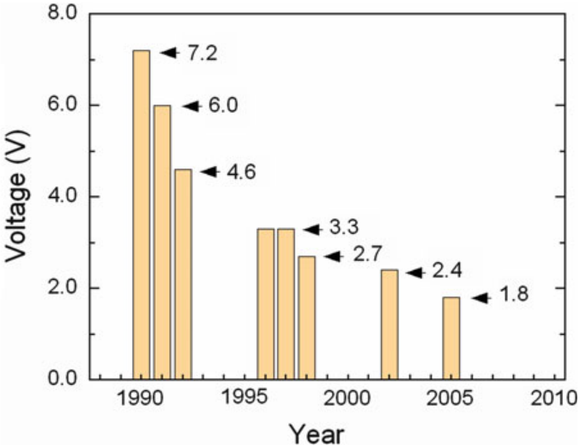

Fig. 1.1 The evolution of the voltage (in volt) at which the semiconductor devices operate in a cellular phone

energy storage is required to power microelectronics, i.e., cell phones and pagers, stand-by power systems. This context has guided the recent evolution of the technology. Figure 1.1 shows the evolution of voltage at which the semiconductor devices operate in a cellular phone. The voltage decrease is related to the thickness of integrated circuits. This picture demonstrates that the powering voltage could reach the range 2–3 V for integrated circuit with a thickness of ~0.2 mm. Of course, this issue led to the design of new batteries for telecommunication devices.

Let us take the case of mobile phones. Most of them today operate on a single cell Li-ion battery, which has a 4.2 V maximum fully charged voltage. Power management system (PMS) is needed because the different components require different voltages: 1.8 V for the digital base band (with a tolerance of ±5 %) and memory, 2.5 V for the analogous base band, 2.8 V for the SIM card and the RF block. The PMS is also acting as a battery management system (BMS) to control the battery charging, monitoring and fuel gauging. From the view point of energy demand of the new generation GSM phone (GSM = Global System for Mobile Communications), the total typical current consumption during talk time is ~275 mA, so that 150 min talk time is available using 700-mAh Li-ion battery. The same device will consume only ~2.25 mA during standby waiting for a call that corresponds a time of 310 h (~13 days) for the same battery [8].

1.4 Energy Storage

In physics, energy is a scalar physical quantity that describes the amount of work that can be performed by a force. During a 1961 lecture for undergraduate students at the California Institute of Technology, Professor Feynman said this about the concept of energy: “There is a fact, or if you wish, a law, governing natural phenomena that are known to date. There is no known exception to this law; it is exact, so far we know. The law is called conservation of energy; it states that there is a certain quantity, which we call energy that does not change in manifold changes which nature undergoes. That is a most abstract idea, because it is a mathematical principle; it says that there is a numerical quantity, which does not change when something happens. It is not a description of a mechanism, or anything concrete; it is just a strange fact that we can calculate some number, and when we finish watching nature go through her tricks and calculate the number again, it is the same" [9].

Excepted geothermal, there are two forms of energy, both of them originating from solar energy: the ancient storage energy, fossil energy, which has been produced during many millions of years and the on-time energy that could be trapped by photovoltaic or wing systems as listed in Table 1.3.

Historically, energy has been stored by containment of raw fuel that is satisfactory for the transportation sector since petroleum; fuel and liquefied gas are portable and readily converted into the desired result: motion. In the electric sector, the necessity to supply energy on demand, which fluctuates weekly and daily, has been accomplished by using different classes of generators in nuclear reactor or firing coal, fuel, gas, biomass. The high cost and limited reserves of oil are forcing a reconsideration of these approaches. Figure 1.2 shows the discharge time vs. energy stored for various energy storage technologies including flywheel, batteries, compressed air, pumped water, hydrogen and gas storage. The use of pumped-hydro is the traditional large scale way to store electricity via gravimetric energy. Both flywheel and batteries are systems capable to deliver the storage energy in few seconds. For instance it has been recently demonstrated that Li-ion batteries including lithium-iron phosphate as positive electrode and lithium titanate as negative electrode can be cycled over 30000 cycles for faster charge rate at 15*C* (4 min), and the discharge rate at 5*C* (12 min) [10]. In practice, it means that a battery made with such cells to power an electric car (EV) will be guaranteed for the life of the

Table 1.3 Classification of energy storage methods

Chemical $\Delta G = \Delta H - T\Delta S$ Hydrogen Biofuels Liquid nitrogen Oxyhydrogen Hydrogen peroxide	Biological Starch Glycogen	Electrochemical Batteries Flow batteries Fuel cells
Electrical $E_{\mathrm{p,e}} = \frac{1}{4\pi\varepsilon_0}\frac{Q_1Q_2}{r}$ Batteries Supercapacitor Superconducting magnetic energy storage	Mechanical $E_{\mathrm{p}} = -\int F dS$ Compressed air Flywheel Hydraulic accumulator Hydroelectric Spring	Thermal $\Delta q = \int C_{\mathrm{v}} dT$ Ice storage Molten salt Cryogenic liquid air Seasonal thermal store Solar pond Steam accumulator Fireless locomotive

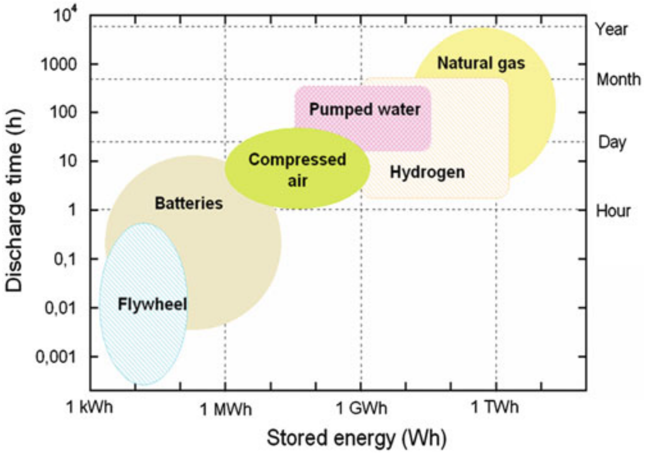

Fig. 1.2 Discharge time vs. energy stored for various energy storage technologies

car, a performance that is expected to boost this market. Note that most of the energy storage systems involve the power-to-gas technology that converts electrical power to gas fuel, including natural and synthetic gas and hydrogen. As shown in Fig. 1.2, time of discharge is very long, which implies the need of grid balancing. Regarding the energy stored requested by consumers, 2 W is needed for cellular phone, while 20–30 W for laptop and 20 kW for electric cars.

Energy storage media are systems storing some form of energy that can be drawn upon at a later time to perform some useful operation. A device that stores energy is sometimes called an accumulator. All forms of energy are either potential energy (e.g., chemical, gravitational or electrical energy) or kinetic energy (e.g., thermal energy). A wind up clock stores potential energy (in this case mechanical, in the spring tension), a battery stores readily convertible chemical energy to keep a clock chip in a computer running (electrically) even when the computer is turned off, and a hydroelectric dam stores power in a reservoir as gravitational potential energy. Ice storage tanks store ice (thermal energy) at night to meet peak demand for cooling. Fossil cells such as coal and gasoline store ancient energy from sunlight. Even food (which is made by the same process as was fossil fuel) is a form of energy stored in chemical form.

Several aspects must be considered for a comparison of energy sources that generate electricity. The first one is the quantity of carbon dioxide equivalent/kWh rejected by energy sources. Figure 1.3 shows the relationship between the CO_2 production and the reaction (response time) for a number of electric power suppliers [11]. It is evident that the response time of nuclear plant (48 h) is bigger than hydro-electric dam or renewable systems such as wind mill and photovoltaic (few seconds). In the middle are the electric power stations using coal, oil or gas.

The second aspect is the gravimetric energy density that is stored (Fig. 1.4a). Let us consider the specific energy available for hydrogen (10^5 Wh kg^{-1}) and gasoline

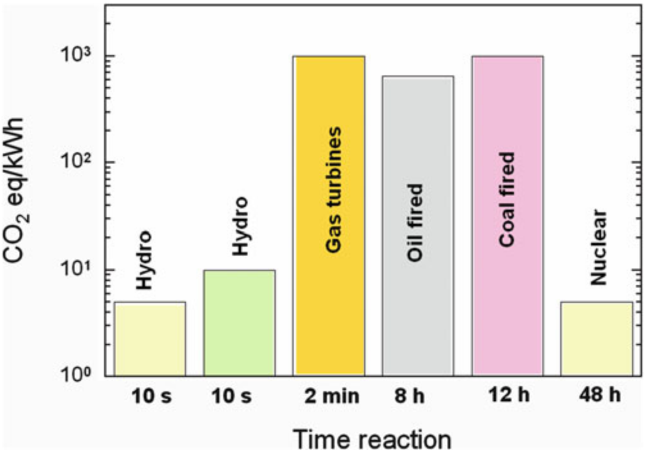

Fig. 1.3 Relationship between the CO_2 production and the time reaction for electric power suppliers

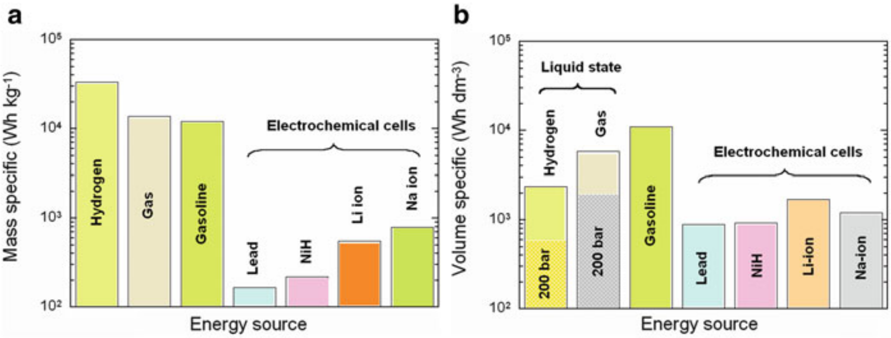

Fig. 1.4 Comparison of various sources of energy (**a**) gravimetric energy density and (**b**) volumetric energy density

(10^4 Wh kg^{-1}). They provide the largest energy density compared to electrochemical cells (~10^3 Wh kg^{-1}), but if a lithium-ion battery is operating for 1000 cycles, we get a total stored energy of ~10^6 Wh kg^{-1} with the same quantity of matter, so that the lithium-ion battery is winning against fossil energies. The third aspect is the volumetric energy density (in Wh dm^{-3}), but the situation is more complex because of the difficulties to store gas and hydrogen by either compression at 200 bar that requires heavy cylinders or by liquefaction that requires cryogenic tanks. Thus, for such a parameter, gasoline is the best source of energy (Fig. 1.4b).

From the foregoing discussion, Birk [12] has suggested three objectives for storage energy, namely: (1) meet discrepancies that can exist between the supplier and the consumer and meet the fluctuating demands for power (it will be the subject of Chap. 19), (2) provide for a more versatile source of energy than can be achieved with the conversion of raw fuels, and (3) change the relative use of the various raw fuels.

1.5 Brief History of Electrochemical Cells

1.5.1 Milestones

Some milestones in electrochemical systems are listed in Tables 1.4 and 1.5 [13, 14]. The history of batteries run from the invention of Alessandro Volta cell in 1800 to the commercialization of Li-ion battery in 1992, via the well-known Leclanché cell, lead-acid battery, nickel-cadmium accumulator and numerous other systems. Generally, the electrochemical cells are classified into two broad categories:

Table 1.4 Primary battery developments

Date	Inventor	Cell design
1000 BC	Baghdad cell	Jar containing an iron rod surrounded by a copper cylinder
1782	Volta	Stack of zinc and silver disks
1813	Davy	First public demonstration of electric lighting
1836	Daniell	$Zn/ZnSO_4/CuSO_4/Cu$
1839	Grove	Nitric acid battery
1866	G. Leclanché	Zinc/manganese dioxide cell
1878	Zinc air cell	$Zn/NaOH/O_2$
1945	Ruben and Mallory	Mercury button-type cell
1949	Lew Urry	Alkaline dry cell commercialized by Eveready Batteries Co.
1961	Silver-zinc cell	$Zn/KOH/Ag_2O$
1970–1980	Lithium-iodine	$Li/Li/I_2$ developed for pace-maker
	Coin cell	Li/aprotic electrolyte/MnO_2
	Li soluble cathode	$Li/SOCl_2$

Table 1.5 Secondary battery developments

Date	Inventor	Cell design
1859	Planté	PbO_2/dilute H_2SO_4/Pb
1899	Waldemar Jungner	Nickel-cadmium cell Ni/2NiOOH/Cd
1905	Edison	Nickel-iron cell Ni/2NiOOH/Fe
1949	Lew Urry	Alkaline dry cell commercialized by Eveready Batteries Co.
1959	Francis Bacon	First practical fuel cell using Ni electrodes
1960s	Volkswagen	Nickel-metal hydride cell with $LaNi_5$ or ZrNi hydrogen sponges
1965	Ford	Beta cell $Na/\beta\text{-}Al_2O_3/S$
1980s	Li polymer	$Li/PEO\text{-}LiClO_4/Ic$ ($Ic=V_6O_{13}$, TiS_2, V_2O_5)[a]
	Microbattery	Li/Li^+ fast ion conductor/TiS_2
1990s	Sony Corp.	Lithium-ion cell based on graphite/$LiCoO_2$ electrodes

[a] *Ic* insertion compound

- *Primary cells* irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the electrochemical cell by electrical means.
- *Secondary cells* can be recharged that is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition.

1.5.2 Battery Designs

Interestingly, researches are still carried on to attain maximum performance and reliability in Leclanché cell [15]. At present, a cell includes several elements for safety because gases are evolved from the manganese dioxide oxidation of the hydrolyzed products formed by the gel (Fig. 1.5). For example, engineers at Rayovac Co. patented a new separator that comprises a Kraft paper separator and a corrosion-inhibiting coating thereupon selected to prevent corrosion of a zinc anode of the Leclanché cell [16].

Batteries design can be compared in view of the three main components; the electrode A, the electrolyte, and the electrode B. A possible battery classification can be deduced from the nature of these components: liquid, soft or solid. This is the figure of the Rubik's cube shown in Fig. 1.6 [13]. All these media can be liquid, plastic (soft) or solid. This is crucial because certain interfaces are difficult to handle. Common batteries have a solid–liquid–solid configuration; the liquid–solid–liquid system corresponds to the Na-S battery using β-alumina as the electrolyte, which permits relatively easy manufacture. On the other side, the all-solid

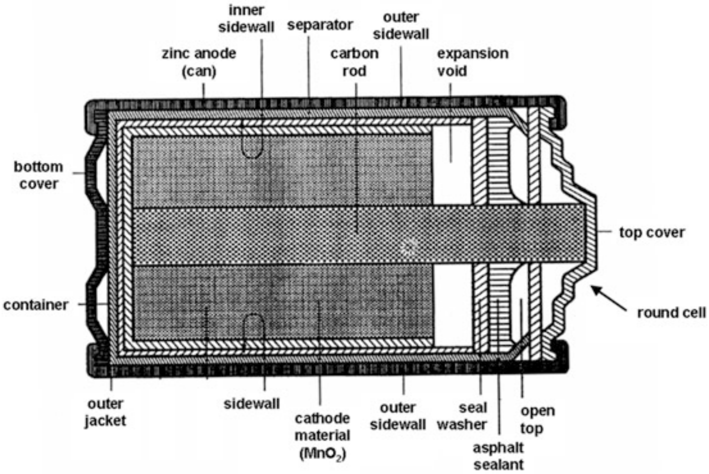

Fig. 1.5 Cross-sectional view of a round Leclanché cell (http://sciencescollege3eme.blogspot.fr/2008/12/histoire-de-pile.htm)

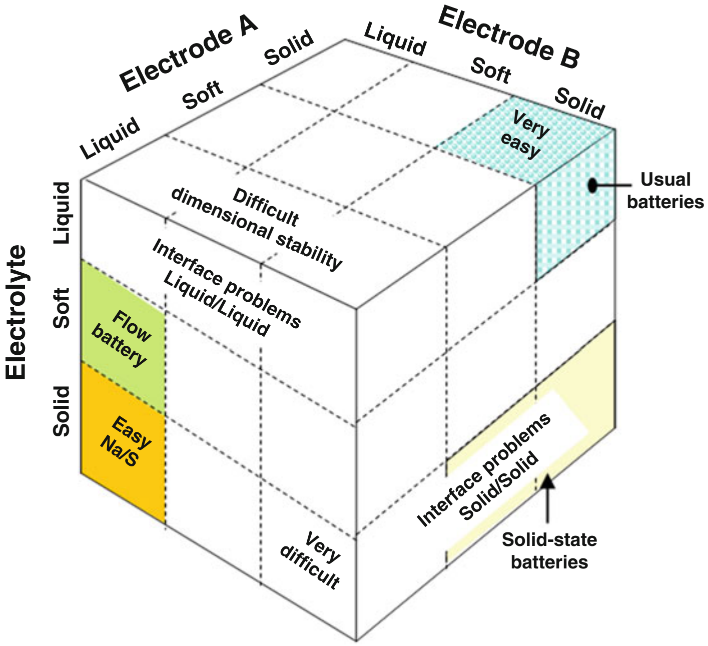

Fig. 1.6 Rubik's cube showing the association of the three components in the solid, soft, and liquid state of electrochemical cells. Reproduced with permission from [13]. Copyright 1994 Wiley

system involves difficult interface problems with crucial dimensional stability at each interface. These difficulties can be solved by using a polymer film as a plastic electrolyte; also, polyethylene oxide (PEO) membranes are the key to Li metal-polymer batteries such as those commercialized by Batscap [17]. Micro-solid state batteries built by successive deposition of thin films partly avoid the interface contact difficulty and can be used as power sources associated to microelectronics [18]. Ultrathin-film solid-state lithium batteries have been fabricated using a thin solid polymer electrolyte membrane prepared by complexion of a plasma polymer and lithium perchlorate [19].

1.6 Key Parameters of Batteries

Battery's users request several high-grades that are long life, high energy density, deep cycle, quick charge and others. With regard to the battery operation, there are several important parameters which are required by consumers: (1) gravimetric specific energy in (Wh g^{-1}), (2) volumetric capacity in (Ah cm^{-3}), (3) rate capability, (4) cyclability (life shelf), and (5) self-discharge. These quantities are fixed by the electrochemical characteristics of the active elements: positive (cathode) and negative (anode) electrodes. Note that in rechargeable batteries the word cathode is not appropriate in terms of electrochemistry because the positive electrode is cathode on discharge and anode on charge, and so forth. A necessary condition in selecting materials for use in batteries is their ability for *redox* properties, i.e., reduction–oxidation reaction, which is more or less the case of almost every inorganic compound in appropriate electrolytes. In addition, one has to select the materials according to key parameters that condition the properties we have listed.

1.6.1 Basic Parameters

Let us discuss the parameters that govern the design of electrochemical power sources. The electrochemical potential, sometimes abbreviated to ECP, is a thermodynamic measure that combines the concepts of energy stored in the form of chemical potential and electrostatics. It is common in both solid-state physics and electrochemistry to discuss the chemical potential and electrochemical potential of an electron. In an electrochemical cell, the chemical reactions take place at the sites of electrodes represented by the generalized relations [20]:

$$\mathrm{a}A + ne \leftrightarrows \mathrm{b}B, \tag{1.1}$$

$$\mathrm{cC} - ne \leftrightarrows \mathrm{d}D, \tag{1.2}$$

$$\mathrm{a}A + \mathrm{c}C \leftrightarrows \mathrm{b}B + \mathrm{d}D, \tag{1.3}$$

where a molecules of A take up n electrons e^{-} to form b molecules of B at one electrode and similarly to the second. Eqs (1.1) and (1.2) express the reduction and oxidation reaction, respectively, and Eq. (1.3) is the overall reaction in the cell given by addition of the two half-cell reaction. The change in the standard free energy, ΔG^0, of this reaction is:

$$\Delta G^0 = -nFE^0, \tag{1.4}$$

where F is Faraday's constant ($F = eN_{\mathrm{A}} = 96485\ \mathrm{C\ mol^{-1}}$) and E^0 is the standard electromotive force (emf) When conditions are other than in the standard state, the potential V_{oc} of the cell is given by the Nernst equation:

$$V_{\mathrm{oc}} = E^0 - \frac{RT}{nF}\ln\frac{\mu^i_{\mathrm{B}}\mu^i_{\mathrm{D}}}{\mu^i_{\mathrm{A}}\mu^i_{\mathrm{C}}}, \tag{1.5}$$

where μ^i is the activity of relevant species, R the gas constant ($8.314\ \mathrm{JK^{-1}\ mol^{-1}}$), and T the absolute temperature.

In the case of two electrodes with a semiconducting character, the *operating voltage* of a cell is limited by the open-circuit voltage, V_{oc}, which is the potential difference across terminals of the battery when no current is being drawn:

$$V_{\mathrm{oc}} = -\frac{1}{nF}\left(\mu_A^i - \mu_C^i\right), \tag{1.6}$$

where $\left(\mu_A^i - \mu_C^i\right)$ is the difference in the chemical potential of the anode (A) and the cathode (C), n is the number of electronic charge involved in the chemical reaction of the cell. The nominal voltage is determined by the energies involved in both electronic and ionic transfer. It is the work function that determines the energy for electron transfer, while the crystallographic structure determines the energy for the transfer of ions. Thus both the electronic band structure and the barrier height for ion motion should be considered. The magnitude of the open-circuit voltage is constrained to $V_{\mathrm{oc}}<5$ V not only by the attainable difference $\mu_A - \mu_C$ of the electrochemical potentials of the anode reductant and the cathode oxidant, but also by either the energy gap E_{g} between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) of a liquid electrolyte, or by the energy gap E_{g} between the top of the valence band and the bottom of the conduction band of a solid electrolyte [21].

The *energy density* is a common measure in evaluating battery systems. Specific energy stored (in Wh kg^{-1}) in a battery is measured by discharging a battery at an appropriate current:

$$E_{\mathrm{pr}} = V_{\mathrm{oc}} Q_{\mathrm{dis}}, \tag{1.7}$$

where V_{oc} is the operating potential in volt (V) obtained from the energy change for the cell reaction and Q_{th} is the specific capacity in ampere-hour per mass (Ah kg^{-1}), or equivalently in mAh g^{-1}. Its theoretical value is obtained from the Faraday'law:

$$Q_{\mathrm{th}} = \frac{1000 \times nF}{3600 \times M_{\mathrm{w}}} = \frac{26.8}{M_{\mathrm{w}}} \times n, \tag{1.8}$$

where M_{w} is the molecular mass of the "limiting" electrode material. As an example, let consider the case of lithium insertion process into the vanadium oxide lattice ($M_{\mathrm{w}} = 542$ g mol^{-1}) that can reversibly accommodate 4Li$^+$ ions per formula unit at an experimental mid-discharge potential 2.4 V vs. Li^0/Li$^+$ at $C/3$ rate according the reaction:

$$4\mathrm{Li}^+ + 4e^- + \mathrm{V_6O_{13}} \leftrightarrows \mathrm{Li_4V_6O_{13}}. \tag{1.9}$$

According to Eq. (1.9), the theoretical specific capacity is 197.8 mAh g^{-1} and the theoretical energy density of 475 Wh kg^{-1}.

The theoretical energy of the battery depends on the capacity of the material and average potential of each electrode material:

$$E_{\mathrm{batt}} = \left(\frac{1}{Q^{+}} - \frac{1}{Q^{-}}\right)^{-1} (E^{+} - E^{-}), \tag{1.10}$$

where Q^{+} and Q^{-} are the capacity of the active materials of the positive and negative electrodes in the battery, respectively.

The C-rate is a parameter used to express the discharge (charge) current in order to normalize the data against the capacity that depends on the battery. A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. A charge at nC rate means a full charge in a time $1/n$ hours [22]. For instance, a $1C$ rate means that the discharge current will discharge the entire battery in 1 h. For a battery with a capacity of 50 Ah, this equates to a discharge current of 50 A. At $C/2$ rate would be 25 A.

The *power output* P_{out} of a battery is the product of the electric current I_{dis} delivered by the discharging battery and the voltage V_{dis} across the negative and positive external contacts:

$$P_{\mathrm{out}} = I_{\mathrm{dis}} V_{\mathrm{dis}}. \tag{1.11}$$

The voltage V_{dis} is reduced from its open-circuit value V_{oc} ($I_{\mathrm{dis}} = 0$) by the voltage drop $I_{\mathrm{dis}}R_{\mathrm{b}}$ due to the internal resistance R_{b} of the battery and the *polarization losses* occur at each electrode and result in a decreased cell potential during discharge (V_{dis}) and an increased cell potential on charge (V_{ch}) that are expressed by:

$$V_{\mathrm{dis}} = V_{\mathrm{oc}} - I_{\mathrm{dis}} R_{\mathrm{b}}, \tag{1.12}$$

$$V_{\mathrm{ch}} = V_{\mathrm{oc}} + I_{\mathrm{ch}} R_{\mathrm{b}}, \tag{1.13}$$

which have the form of Ohm's law. In addition the Joule heating effect of the I^2R_{b} losses in the internal resistance of the cell will rise the temperature. It follows from Eqs. (1.11) and (1.13) that realization of a high maximum power $P_{\max}$ requires, in addition to as high a V_{oc} as possible, a low internal battery resistance R_{b} expressed by:

$$P_{\max} = I_{\max} V_{\max}, \tag{1.14}$$

$$R_{\mathrm{b}} = R_{\mathrm{e1}} + R_{\mathrm{in}}(A) + R_{\mathrm{in}}(C) + R_{\mathrm{c}}(A) + R_{\mathrm{c}}(C), \tag{1.15}$$

where $R_{\mathrm{in}}(A)$, $R_{\mathrm{in}}(C)$ are the resistances to transport of the working ion across the electrolyte–electrode interface and $R_{\mathrm{c}}(A)$, $R_{\mathrm{c}}(C)$ are the intrinsic resistance of electrodes. The electrolyte resistance R_{e1} to the ionic current is proportional to the ratio of the effective thickness L to the geometrical area A of the inter-electrode space that is filled with an electrolyte of ionic conductivity σ_i as:

$$R_{\mathrm{el}} = \frac{L}{A\sigma_i}. \tag{1.16}$$

The resistance to transport of the working ion across the electrolyte–electrode interfaces is proportional to the ratio of the geometrical and interfacial areas at each electrode:

$$R_{\mathrm{in}} \sim A/A_{\mathrm{in}}. \tag{1.17}$$

Since the chemical reaction of the cell involves ionic transport across an interface, Eq. (1.17) dictates the construction of a porous, small-particle electrode. Achievement and retention of a high electrode capacity, i.e., use of a high fraction of the electrode material in the reversible reaction, requires the achievement and retention of good electronic contact between particles as well as a large particle–electrolyte interface area over many discharge–charge cycles. If the reversible reaction involves a first-order phase change, the particles may fracture or lose contact with one another upon cycling, breaking a continuous electronic pathway to the current collector.

The battery voltage V_{dis} vs. the discharge current I_{dis} delivered across a load is called the polarization curve. The voltage drop $(V_{\mathrm{oc}} - V) = \eta(I)$ of a typical curve (Fig. 1.7) is a measure of the battery resistance:

$$R_{\mathrm{b}}(I) = \eta(I)/I. \tag{1.18}$$

On charging, $\eta(I_{\mathrm{ch}}) = (V_{\mathrm{ch}} - V_{\mathrm{oc}})$ is referred to as an overvoltage. The interfacial voltage drops saturate in region (I) of Fig. 1.7; therefore in region (II) the slope of the curve is:

$$dV/dI \approx R_{\mathrm{el}} + R_{\mathrm{c}}(A) + R_{\mathrm{c}}(C) \tag{1.19}$$

Region (III) is diffusion-limited; at the higher currents, normal processes do not bring ions to or remove them from the electrode–electrolyte interfaces rapidly enough to sustain an equilibrium reaction. The battery voltage V vs. the state of charge, or the time during which a constant current I has been delivered, is called a discharge curve.

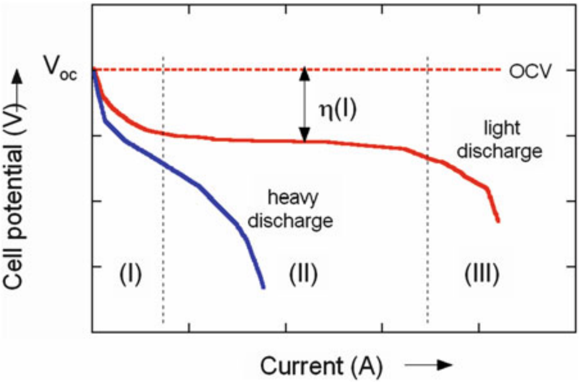

Fig. 1.7 Typical polarization curve for the battery voltage V vs. the I delivered across a load. The voltage drop $(V_{\mathrm{oc}} - V) = \eta(I)$ of a typical curve is a measure of the battery resistance $R_{\mathrm{b}}(I)$

The state-of-charge (SOC) of a battery is the fraction (in %) of available charge capacity to the total capacity of the battery:

$$\mathrm{SOC} = 100\% - \frac{Q_\mathrm{e}}{Q_0}, \tag{1.20}$$

where Q_e is the battery charge and Q_0 the nominal battery capacity (in Ah). The SOC of a battery is the main parameter because the user needs to know the remaining available energy before the next charge. The knowledge of SOC is very challenging; that requires battery modelling [23, 24].

The *self-discharge rate* (SDR) is the percentage of capacity that a battery loses in open-circuit conditions. From usual terms, the SDR is estimated from the lost discharge capacity after 2 days storage in normal conditions to the maximum cell capacity as:

$$\mathrm{SDR}(\%) = \frac{Q_\mathrm{max} - Q_\mathrm{ret}}{Q_\mathrm{max}} \times 100\%, \tag{1.21}$$

where Q_max is the maximum discharge capacity at a discharge current density C/n and Q_ret the retained capacity at a discharge C/n rate. As an example, experimental profiles of charge–discharge for a $\mathrm{Li//LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2}$ cell operating at various C-rate are illustrated in Fig. 1.8.

1.6.2 Cycle Life and Calendar Life

Usually, the aging of the battery performance has two origins: (1) the *cycle fade* and (2) the *calendar fade* that is the elapsed time before the battery is not usable at all. An increase in the temperature whether the battery is in active use or not and an increase of the SOC severely affect the degree of degradation. The net result is an increase of the internal resistance and capacity loss $L(t)$, which can be expressed by an empirical law as [25]:

$$L(t) = A\sqrt{t}, \tag{1.22}$$

where A is a constant. Electrochemical impedance spectroscopy (EIS) is a powerful tool to determine the interfacial resistance of a cell as a function of temperature, state-of-charge (SOC) and cycle number [26]. Equation (1.22) yields the formation of the passivation film at the electrode surface. The solvent diffusion model presented by Ploehn et al. [25] predicts, in all cases, passivation films growing to several tens of nanometers in thickness over time periods in excess of 1 year under float potential conditions (the float potential is the voltage at which a battery is maintained after being fully charged to maintain its capacity by compensating for

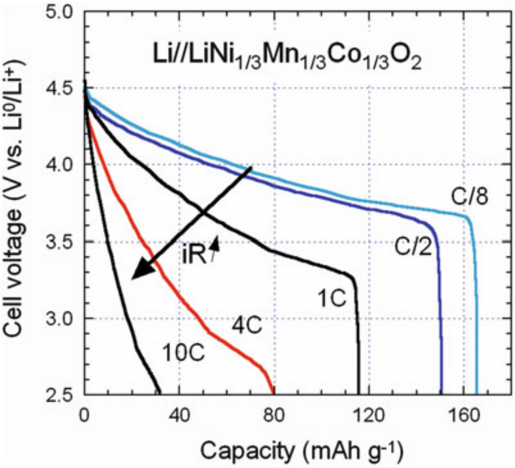

Fig. 1.8 Discharge curves for a Li//LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell operating at various *C*-rates

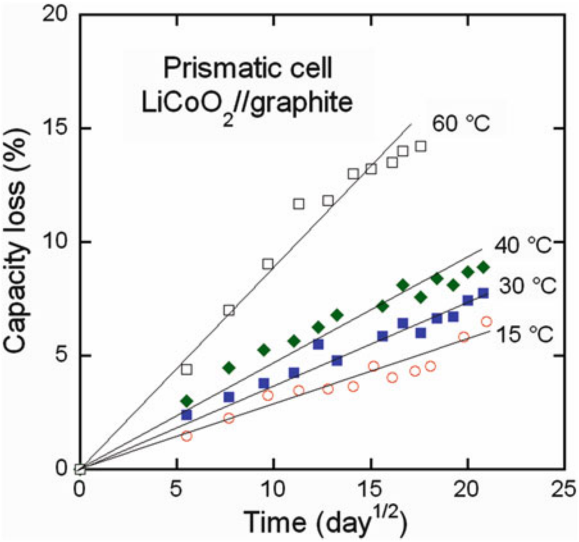

Fig. 1.9 Capacity fade of a prismatic LiCoO$_2$//synthetic graphite cell with 1 mol L^{-1} LiPF$_6$ in solvent EC:DEC: DMC as electrolyte. The cell was stored at different temperatures in the range 15–60 °C at float potential of 3.8 V. Reproduced with permission from [25]. Copyright 2004 The Electrochemical Society

self-discharge). Figure 1.9 illustrates the time evolution of the capacity fade for a prismatic prototype cell LiCoO$_2$//synthetic graphite stored a float potential of 3.8 V.

The *cycle life* corresponds to the number of charge–discharge processes a battery can fulfill before its nominal capacity falls below 80 %. The relationship between cycle life and depth-of-discharge (DOD) appears to be logarithmic. The *shelf life* is the time spent before a battery is out of use during storage. Wright et al. [27] presented the tests and analysis of the capacity fade resulting from the cycle life experiments at 25 and 45 °C for 18650-sized Li-ion batteries including LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode materials. The number of test cycles for up to 44 weeks were 369000 cycles at 1*C* and *C*/25 discharge rate. Broussely et al. [26]

studied the long-term calendar life of Li-ion cells containing either $LiCoO_2$ or $LiNi_yMn_{1-y}O_2$ cathodes tested in the temperature range 15–60 °C.

The *coulombic efficiency*, CE in %, is the ratio between the discharge capacity and the charge capacity for each cycle:

$$\mathrm{CE}(\%) = \frac{Q_{\mathrm{disch}}}{Q_{\mathrm{ch}}} \times 100\%, \tag{1.23}$$

thus the rate of capacity loss is inverse proportional to the duration of the test, t_{ts}, given by:

$$\psi = \frac{1 - \mathrm{CE}}{t_{\mathrm{ts}}}, \tag{1.24}$$

The rate of capacity loss is representative of numerous effects such as the growth of the solid electrolyte interphase (SEI) layer, the aging of the crystallographic structure of electrode materials, impurities dissolved in the electrolyte, unwanted chemical reactions, side effects, and generation of other compounds.

1.6.3 Energy, Capacity and Power

1.6.3.1 Modified Peukert Plot

How long does a battery last? The problem with quantifying the stored specific capacity is its discharge rate dependence. The faster the discharge C-rate, the lower remaining capacity, so a battery rated for 120 Ah actually provides a lower capacity when drained at rate higher than $C/20$ that is the typical rate for a lead acid battery (PbBat). The lithium-nanophosphate (Li-nP) chemistry exhibits this effect to a much lesser extent. These two batteries are equivalent at rate $C/20$. At faster rate, however, the Li-nP battery demonstrates higher capacities than PbBats. A Li-nP battery rated at 120 Ah will deliver 114 Ah when discharge at $1C$ rate, or 95 % of the rated capacity; in similar conditions a PbBat provides only 88 Ah [28]. Thus, calculating the discharge of a 120-Ah battery will run 12 h under a 10 A load is a false notion of order. This phenomenon can be considered using the Peukert's law (from the name of the German engineer who tested lead acid batteries), which is the simplest model for predicting battery lifetimes taking into account part of the nonlinear properties of the battery. The modified Peukert formula figures the discharge current I_n (in A) into the relation [29]:

$$I_n^k t = \Gamma, \tag{1.25}$$

where t is the maximum discharge time (in A), k is the Peukert exponent that is different from a battery to another one and Γ is a constant. From the derivation of

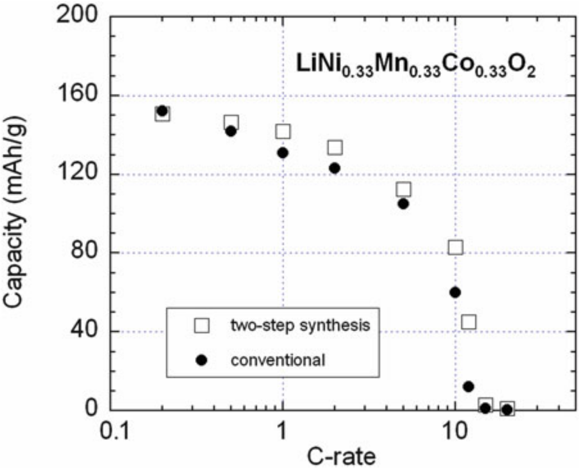

Fig. 1.10 Modified Peukert plots of the Li//$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cells using solution 1 mol L^{-1} $LiPF_6$ in EC-DEC as electrolyte. Cells were cycled between 2.5 and 4.5 V vs. Li^0/Li^+. Cathode materials were synthesized by (**a**) the conventional wet-chemical method assisted by oxalic acid and (**b**) the two-step oxalate route. Reproduced with permission from [30]. Copyright 2012 Springer

the Eq. (1.21), the available capacity Q_m at different discharge rate I_{m1} is expressed by [29]:

$$Q_m = Q_n \left(\frac{I_n}{I_m}\right)^{k-1}. \tag{1.26}$$

The total discharge time will be *m* hours. For flooded lead acid batteries it ranges as $1.2 \le k \le 1.6$, while Ni-MH batteries have a smaller value of *k,* and that of Li-ion batteries is even better. The Peukert exponent is generally affected by several factors, among them the temperature and the age of the battery. Figure 1.10 shows the modified Peukert plot for Li cells including $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) electrode materials synthesized by different routes. The tests were carried out after five cycles under the same conditions. The Peukert analysis evidences the difference between the powders synthesized using the conventional wet-chemistry assisted by oxalic acid, which results in a material with 3.2 % cationic disorder (fraction of Ni^{2+} on the 3*b* Li sites), and the two-step oxalate method for which $Ni^{2+}(3b) = 2.6$ %. It is obvious that the lower cationic disorder improves the capacity retention: even at the high rate of 10*C*, the capacity reversible capacity was 83 mAh g^{-1}, which is 50 % of the initial discharge capacity [30].

1.6.3.2 Ragone Figure

The Ragone concept is based on the equivalent circuit of an electrical storage system connected to a load or a generator. The battery can be modeled by a pure power source of uniform potential V_{oc} in series with the internal resistance, R_s, generating ohmic losses when the current *i* draws the load represented by the resistance R_L so that the potential across the load is given by the basic Ohm's law:

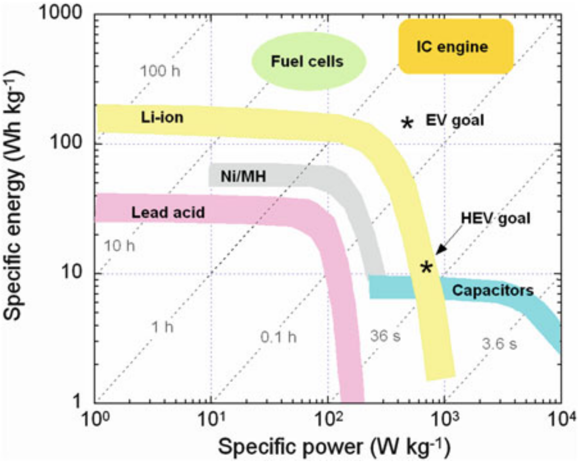

Fig. 1.11 Ragone charts of various electrochemical energy-storage devices. Association of Li-ion batteries and supercapacitors should provide a significant impact on performance of electrical vehicles: acceleration and long range

$$V_{\mathrm{dis}} = R_{\mathrm{L}} i. \tag{1.27}$$

Combining Eqs. (1.12) and (1.27), the cell voltage is given by:

$$V_{\mathrm{oc}} = V_{\mathrm{L}} \left(1 + \frac{R_{\mathrm{S}}}{R_{\mathrm{L}}} \right). \tag{1.28}$$

We can distinguish different energy terms: the energy W_{L} that is supplied to the load and the energy W_{s} that is dissipated in heat by the internal resistance [31, 32]. Currently, Ragone chart is plotted with log-log scales of the available specific energy (in Wh kg^{-1}) against specific power (in W kg^{-1}). Volumetric quantities are also considered in the case of electrochemical capacitors [33]. Figure 1.11 illustrates the Ragone plots of various electrochemical energy-storage devices [34]. It is shown that capacitors have higher specific power but modest specific energy compared to batteries. In terms of transportation, capacitors offer good acceleration but poor range; it is opposite for batteries [35].

1.7 Electrochemical Systems

1.7.1 Batteries

The main electricity storage options appropriate to power any modern system are: (1) electrochemical devices (batteries) using chemical reactions to generate power, (2) hydrogen production, compression, storage and power generation through fuel cells and (3) super-capacitors and ultra-capacitors that store energy in the form of accumulated charge. In this section, we briefly compare batteries and supercapacitors (commonly names "supercaps") [36]. The main targeted technology is the obtaining of devices both smaller and lighter, which are the typical qualities requested for portable and electric transportation systems. Figure 1.12 displays various electrochemical systems in a plot of specific volumetric energy against gravimetric volumetric energy.

Electrochemical batteries are currently classified into different classes from the view point of the principle, nature of components (see Fig. 1.6), design and working conditions: nonrechargeable (primary) vs. rechargeable (secondary) systems (Table 1.6); aqueous vs. nonaqueous cells; liquid vs. solid electrolyte cells; low vs. high temperature batteries, etc. Since a battery has its own properties according the chemistry used for electrodes and electrolyte, the characterization of all the parameters is requested by consumers. For instance, zinc/silver oxide batteries developed by the US Navy for powering torpedo provide the highest energy per unit weight and volume among any commercially available aqueous secondary battery system. Note that lead-acid batteries are the most popular low cost secondary batteries produced worldwide so far; they represent approximately 45 % of the

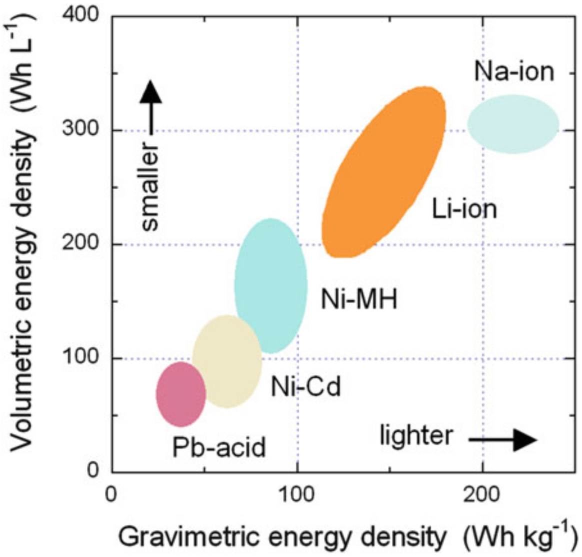

Fig. 1.12 Figures of merit of electrochemical batteries

Table 1.6 Classification of batteries

	Aqueous cell	Nonaqueous cell
Primary battery	Manganese dry cell	Metallic lithium battery
	Alkaline dry cell	
	Magnesium cell	
Secondary battery	Lead-acid battery	Li polymer battery
	Ni-Cd battery	Li-ion battery
	Ni-MH battery	

sales volume of all electrochemical systems. Characteristics of primary and secondary battery systems with their reaction mechanism can be found in Refs. [37, 38].

Batteries as energy storage systems (ESS) are essential for electric drive vehicles, such as hybrid electric vehicles (HEVs) plug-in hybrid electric vehicles (PHEVs) and all-electric vehicles (EVs). HEVs used currently Ni-MH batteries, which show longer life cycle than lead-acid batteries. Despite their high cost, lithium-ion batteries with an adequate chemistry (lithium-phosphate is the most popular) are powering PHEVs and EVs. Supercapacitors can provide additional power to vehicles (see Fig. 1.11) during acceleration and hill climbing. Supercaps are also used as devices to recover braking energy and to assist level load power of batteries. According the US Office of Energy Efficiency & Renewable Energy as part of the Department of Energy (DOE), the transition to a light-duty fleet of HEVs and EVs could reduce US foreign oil dependence by 30–60 % and greenhouse gas emissions by 30–45 % dependent of the exact mix technologies. The "EV Everywhere Blueprint" program gives the 10-year vision of DOE for plug-in electric vehicles (PEVs). The goals is the lowering cost of electric drive batteries from $500 to $125/kWh, and increasing density from 100 to 250 Wh kg^{-1}, 200 to 400 Wh L^{-1}, and 400 to 2000 W kg^{-1}. Note that, in the USA, 97000 PEVs were sold in 2013 [39]. The mission of the US Advanced Battery Consortium LLC (USABC), a collaborative organization operated by the three US car industries, Chrysler Group LLC, Ford Motor Company, and General Motors, is the development of electrochemical storage technologies that support commercialization of fuel cell, hybrid and electric vehicles, with the goal of reduction cost to $20/kW and extend life to 15 years. The total funding of USABC was $21.6 million in 2012 [40].

1.7.2 Electrochromics and Smart Windows

Electrochromic devices act to modulate incident radiation via transmission, absorption, or reflection of the light. Typically, an electrochromic device can be thought of a series of five thin films deposited on glass: a transparent conductor, an electrochromic material (working electrode), an ion conductor (separator/electrolyte), an electrochromic material (counter-electrode) and a transparent conductor (Fig. 1.13). By applying an electric field across the electrodes, the optical transmission and/or reflection of the working electrode can be modulated with a dynamic control of the radiation. The electrodes used in the devices are dependent of the type of device: absorptive/transmissive or absorptive/reflective [41]. Although, working electrode materials include WO_3, MoO_3, NiO, Ni_2O_3, In_2O_3, SnO_2:Sn, SnO_2:F, VO_2, PEDOT/PSS, single-walled carbon nanotubes (SWNT), etc. [42]. The optical modulation is due to the reduction or oxidation of the electrode material that allows reversible insertion/extraction of ions (proton, Li^+, Na^+) into/from its host lattice. Upon insertion, the host changes its color, which makes possible an electrochromic display or a smart window. For example, white-transparent WO_3 film associated

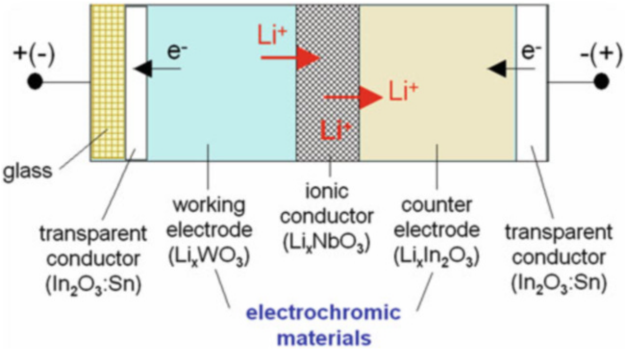

Fig. 1.13 Schematic view of an electrochromic device

with an acidic electrolyte can be used in an electrochromic display according to the reversible reaction:

$$xH^+ + xe^- + WO_3 \leftrightarrow H_xWO_3, \tag{1.29}$$

that products a dark-blue tungsten bronze, H_xWO_3, with the reduction of the transition metal from W^{6+} to W^{5+} [43]. Note that similar electron transfer occurs for lithium insertion. In practice, small cations such as H^+ and Li^+ can be easily inserted into the layered compounds and in the tunnel-like frameworks as well [44].

In any structure, traditional windows are the largest consumer of energy. Commonly, metallic coatings that reflect light and heat are used but they are not versatile and cannot be adjusted. Low-energy glasses named *smart windows* (introduced in the late 1990s) are based on paired electrochromic reactions that change light and heat transmission properties in response to voltage. They are automatically monitored when the exterior environment goes above the transition temperature. This type of low-power consuming technology could potentially save billions of dollars on heating, cooling, and lighting costs. The DOE estimates that windows currently cost $40 billion a year in energy use, which amounts to one quarter of the total energy spent in the USA. [45]. A smart window is composed of two standard float glasses (one has an electrochromic coating applied on one of the surfaces) sealed to form a single insulating glass unit (IGU) with an air space between each slice. The coating provides selective control over visible light and heat-producing near-infrared (NIR) light. Recently researchers reported the introduction of tin-doped indium oxide nanocrystals into niobium oxide glass (NbO_x), and realized a new amorphous structure as a consequence of linking it to the nanocrystals. Unprecedented optical switching and excellent electrochromic stability, with 96 % of charge capacity retained after 2000 cycles were demonstrated [46]. Smart windows are currently in use in architectures (commercial, office, private); Boeing has used them on its new "787 Dreamliner" aircraft.

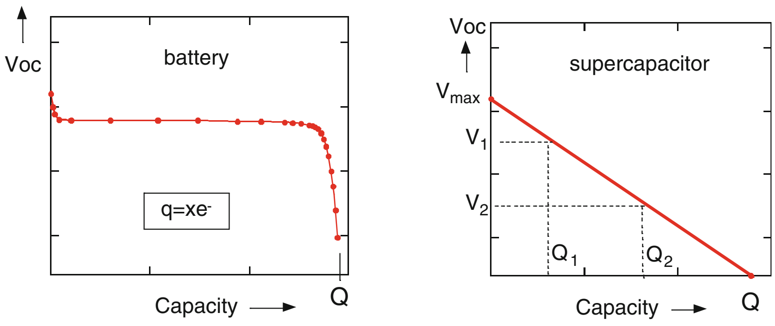

Fig. 1.14 V_{oc} vs. capacity of battery and supercapacitor

1.7.3 Supercapacitors

Supercapacitors, also known as electric double-layer capacitors (EDLCs) or ultracapacitors, have a high energy density when compared to conventional electrolytic capacitors. Larger supercaps have capacitance up to 5000 F. [47]. For applications in which significant energy is needed in pulse form, traditional capacitors used in electronic circuits cannot store enough energy in the volume and weight available. For these applications, the development of high energy density capacitors has been undertaken by various groups around the world [48]. Figure 1.14 shows the fundamental difference between V_{oc} of a battery compared to that of supercap. The simplest capacitors store energy by charge separation in a thin layer of dielectric material that is supported by metal plates that act as the terminals for the device. The energy stored in a capacitor is given by $1/2CV^2$, where C is its capacitance and V is the voltage between the plates. The capacitance value is calculated using the following expression:

$$C = \frac{\Delta Q}{\Delta V} = \frac{I \Delta t}{\Delta V}, \tag{1.30}$$

where I is the constant discharging current, $\Delta t = t_2 - t_1$ and $\Delta V = V_1 - V_2$, $V_1 = 80\ \%\ V_{max}$, $V_2 = 40\ \%\ V_{max}$ and V_{max} is the maximum voltage of the supercapacitor.

In an ultracapacitor, the electrodes are fabricated from high surface area, porous material having pores of diameter in the nanometer range. There are: activated carbon black, aerogel carbon, anhydrous RuO_2, transition-metal oxides (for instance MnO_2) or doped conducting polymers providing capacitance in the range 100–1300 F cm^{-3}. Projections of future developments using carbon indicate that energy densities of 10 mWh g^{-1} or higher are likely with power densities of 1–2 W g^{-1}.

1.8 Concluding Remarks

In this chapter, we have evoked briefly the fundamentals of the storage energy that are daily applied to face the problems associated with the use of fossil fuels (oil, gas and coal), the release of greenhouse gases and the devastating effects of raising the planet temperature as well. Also, energy can be stored in different forms having their own technologies. The use of electricity as power source requests new devices. Several examples can be cited. Electricity production from renewable energy sources needs to store electricity when lack of sunshine or wind is experienced. The integration of these new primary sources requires more attention in the design, control and management of the electric grid. Less-polluting automobiles necessitate the replacement of electric energy for oil. This is a great challenge because of the need of efficient, cheap and reliable batteries. Behind such a technology, the field of storage energy constitutes a multidisciplinary research of modern material science, including the development of new concepts. These days, there is a considerable global research activity on materials related to insertion reactions that constitute a breakthrough in extended applications, with the synthesis of these multi-component devices for storage energy. The fascination with electrical energy storage is driven by the potential superior performance of materials, by environmental necessity, and by the fundamental challenges these technologies present.

The most advanced technology for energy storage uses advanced materials and high performing systems include metal-hydride batteries, lithium-ion batteries, electrochromics, supercaps, etc., all of them need to be optimized for higher specific energy and power requirements. Recently, application of the nanotechnology to storage systems and especially in batteries and supercaps has opened the way for novel enterprise. For instance, lithium-ion batteries are used in large facilities to support energy storage, the load leveling and frequency regulation. With the ability to inject electricity contained in the batteries of cars on the grid, the Vehicle-to-Grid (V2G) technology will emerge.

References

1. El-Ashry M (2010) Renewvable energy policy network for the 21st century. http://www.harbortaxgroup.com/wp-content. Accessed Sept 2010
2. The European Wind Energy Association (2014) Wind in power 2013 European statistics. http://www.ewea.org/fileadmin/files/library/publications/statistics/EWEA_Annual_Statistics_2013.pdf. Accessed Feb 2014
3. Schneider EL, Oliveira CT, Brito RM, Malfatti CF (2014) Classification of discarded MIMH and Li-ion batteries and reuse of the cells still in operational conditions in prototypes. J Power Sourc 262:1–9
4. Van Noorden R (2014) A better battery. Nature 507:26–28
5. International Energy Agency (IEA) (2014) http://www.iea.org/statistics

6. European Environment Agency (2013) Atmospheric greenhouse gas concentrations. http://www.eea.europa.eu/data-and-maps/indicators/atmospheric-greenhouse-gas-concentrations-3/assessment. Accessed Feb 2014
7. Zaghib K, Guerfi A, Hovington P, Vijh A, Trudeau M, Mauger A, Goodenough JB, Julien CM (2013) Review and analysis of nanostructured olivine-based lithium rechargeable batteries: status and trends. J Power Sourc 232:357–369
8. Szepesi T, Shum K (2002) http://www.eetimes.com/document.asp?doc_id=1225408. Accessed 20 Feb 2002
9. Feynman R (1964) The Feynman lectures on physics, vol 1. Addison Wesley, New York
10. Zaghib K, Dontigny M, Guerfi A, Charest P, Mauger A, Julien CM (2011) Safe and fast-charging Li-ion battery with long shelf life for power applications. J Power Sourc 196:3949–3954
11. ITM Power (2014) www.itm-power.com
12. Birk JR (1976) Energy storage, batteries, and solid electrolytes: prospects and problems. In: Mahan GD, Roth WL (eds) Superionic conductors. Plenum, New York, pp 1–14
13. Julien C, Nazri GA (1994) Solid state batteries: materials design and optimization. Kluwer, Boston
14. Julien C, Nazri GA (2001) Intercalation compounds for advanced lithium batteries. In: Nalwa HS (ed) Handbook of advanced electronic and photonic materials, vol 10. Academic Press, San Diego, pp 99–184, chap 3
15. Augustynski J, Dalard F, Machat JY, Sohm JC (1975) Electric cells of the Leclanché type. US Patent 3,902,921, 2 Sept 1975
16. Ekern RJ, Armacanqui ME, Rose JI (1997) Reduced environmental hazard Leclanché cell having improved performance ionically permeable separator. US Patent 5,604,054, 18 Feb 1997
17. Bascap (2009) http://www.batscap.com. Accessed 5 Mar 2009
18. Julien C (1997) Solid state batteries. In: Gellings PJ, Bouwmeester HJM (eds) The CRC handbook of solid state electrochemistry. CRC Press, Boca Raton, pp 372–406
19. Ogumi Z, Uchimoto Y, Takehara Z, Kamanori Y (1988) Thin all-solid-state lithium batteries utilizing solid polymer electrolyte prepared by plasma polymerization. J Electrochem Soc 135:2649–2650
20. Weppner W, Huggins R (1977) Determination of the kinetic parameters of mixed-conducting electrodes and applications to the system Li_3Sb. J Electrochem Soc 124:1569–1578
21. Goodenough JB, Kim Y (2010) Challenges for rechargeable Li batteries. Chem Mater 22:587–603
22. Julien CM, Mauger A, Zaghib K, Vijh A (2010) Lectures of the workshop on materials science for energy storage, Chennai, India, 18–22 Jan 2010
23. Linden D, Reddy TB (2001) Handbook of batteries, 3rd edn. McGraw-Hill, New York
24. Bergveld HJ, Kruijt WS, Notten PHL (2002) Battery management systems, design by modelling. Kluwer Academic Publishers, Dordrecht
25. Ploehn HJ, Ramadass P, White RE (2004) Solvent diffusion model for aging of lithium-ion battery cells. J Electrochem Soc 151:A456–A462
26. Broussely M, Herreyre S, Biensan P, Kasztejna P, Nechev K, Staniewicz RJ (2001) Aging mechanism in Li ion cells and calendar life predictions. J Power Sourc 97–98:13–21
27. Wright RB, Christopherden JP, Motloch CG, Belt JR, Ho CD, Battaglia VS, Barnes JA, Duong TQ, Sutula RA (2003) Power fade and capacity fade resulting from cycle-life testing of advanced technology development program lithium-ion batteries. J Power Sourc 119–121:865–869
28. Mike M, Les A, Knakal T (2011) Lithium ion vehicle start batteries, power for the future. In: Proc NDIA ground vehicle systems engineering and technology symposium, Dearborn, MI, Accessed 9–11 Aug 2011
29. Doerffel D, Sharkh SA (2006) A critical review of using the Peukert equation for determining the remaining capacity of lead-acid and lithium-ion batteries. J Power Sourc 155:395–400

30. Hashem AM, El-Taweel RS, Abuzeid HM, Abdel-Ghany AE, Eid AE, Groult H, Mauger A, Julien CM (2012) Structural and electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material prepared a two-step synthesis via oxalate precursor. Ionics 18:1–9
31. Gallay R (2014) Energy storage. Ragone. http://www.garmanage.com/atelier/index.cgi?path=public/Energy_storage/Ragone
32. Christen T, Carlen MW (2000) Theory of Ragone plots. J Power Sourc 91:210–216
33. Pech D, Brunet M, Durou H, Huang P, Mochalin V, Gogotsi Y, Taberna PL, Simon P (2010) Ultrahigh-power micrometer sized supercapacitors based on onion-like carbon. Nat Nanotechnol 5:651–654
34. Srinivasan V (2011) The three laws of batteries and a bonus Zeroth law. http://gigaom.com/2011/03/18/the-three-laws-of-batteries-and-a-bonus-zeroth-law. Accessed 18 Mar 2011
35. Scherson DA, Palencsar A (2006) Batteries and electrochemical capacitors. Interface Spring 2006:17–22
36. Winter M, Brodd RJ (2004) What are batteries, fuel cells and supercapacitors? Chem Rev 104:4245–4269
37. Linden D, Reddy T (2002) The handbook of batteries, 3rd edn. The McGraw-Hill, New York
38. Colin V, Scrosati B (1997) Modern batteries, 2nd edn. Wiley, Portland
39. Office of Energy Efficiency & Renewable Energy (2014) http://energy.gov/eere/vehicles/vehicle-technologies-office-batteries. Accessed July 2014
40. Snyder K (2012) Overview and progress of United States Advanced Battery Consortium (USABC) activity. http://www1.eere.energy.gov/vehiclesandfuels/pdfs/merit_review_2012/energy_storage/es097_snyder_2012_o.pdf. Accessed 15 May 2012
41. Granqvist CG, Azens A, Hjelm A, Kullman L, Niklasson GA, Rönnow D, Mattsson MS, Veszelei M, Vaivars G (1998) Recent advances in electrochromics for smart windows applications. Sol Energ 63:199–216
42. Niklasson GA, Granqvisr CG (2006) Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these. J Mater Chem 17:127–156
43. Cogan SF, Plante TD, Parker MA, Rauh RD (1986) Free-electron electrochromic modulation in crystalline Li_xWO_3. J Appl Phys 60:2735–3738
44. Castro-Garcia S, Pecquenard B, Bender A, Livage J, Julien C (1997) Electrochromic properties of tungsten oxides synthesized from aqueous solutions. Ionics 3:104–109
45. Hatt A (2013) Raising the IQ of smart windows. http://www.eurekalert.org/pub_releases/2013-08/dbnl-rti081413.php. Accessed 14 Aug 2013
46. Llordés A, Garcia G, Gazquez J, Milliron DJ (2013) Tunable near-infrared and visible-light transmittance in nanocrystal-in-glass composites. Nature 500:323–326
47. Al-Sakka M, Gualous H, Omar N, Van Mierlo J (2012) Batteries and supercapacitors for electric vehicles. http://cdn.intechopen.com/pdfs-wm/41417.pdf
48. Burke A (2000) Ultracapitors: why, how, and where is the technology. J Power Sourc 91:37–50