Knowledge related to electric charges is considered as old as human history. For example, in approximately 600 BC, Thales of Milet described the phenomena when rubbing amber as electrostatic charging. The generation of electric charges (more precisely, charge separation) and the phenomena caused by charges of the same or opposite signs have been the subject of curiosity and scientific investigation for several centuries. However, such studies have been limited by an inherent problem: the storage of electricity, i.e. electric charge. Some condenser-like devices, e.g. the Leyden flask (1745), had very limited capacity, and similar condenser-based contraptions did not help very much. Only recently (starting with a patent in 1957), the principle of the condenser has been developed resulting in novel devices: the supercap(acitor) and the ultracap (see Chapter 11).

In 1800 Alessandro Volta discovered that placing zinc and silver plates close to each other with a piece of brine-soaked pasteboard in between produces an electric voltage. This became the first source of continuous supply of electricity and the device is still called a voltaic cell. Placing many of those sandwich-like devices on top of each other resulted in a multiplied electric voltage because of the serial connection - the Volta-pile. For quite some time this device together with the Daniell element (1836) was the only source of electricity providing a continuous flow of current compared to the short-lived discharge current from any condenser, which was popularly used in telegraphic systems in the 1850s. The French physicist Gaston Planté constructed the first lead-acid accumulator in 1859. Waldmar Jungner (1899) discovered the nickel-cadmium accumulator, which was substantially improved up to the point of commercialization by the invention of porous electrodes by Schlecht and Ackermann in 1932. Complete sealing of the cell enabled by changes in cell and electrode setup provided by Neumann in 1947 yielded the secondary batteries very popular in numerous applications until recently, when the toxicity of cadmium was identified as a major problem and when suitable substitutes for the cadmium electrode were reported. The discovery of huge hydrogen storage capabilities by intermetallic compounds such as SmCo₅ and LaNi₅ provided a nontoxic substitute for the cadmium electrode, with the resulting NiMH accumulator replacing NiCd accumulators in many applications. Finally lithium-ion batteries were successfully commercialized in 1991 after initial failures of secondary lithium batteries utilizing metallic lithium electrodes.

1

The development of the dynamoelectric principle and the invention of a first electric generator by Werner (von) Siemens (1866) enabled engineers in the 1850s to solve problems dealing with electric cars and more generally with the utilization of electric energy. Now electricity could be generated by converting mechanical energy derived from a multitude of sources by coupling this source in a suitable way to the generator. Although not quite clear from the beginning, alternating current (AC) rapidly gained commercial importance and has been preferred than direct current (DC). Because both power and energy of batteries had always been limited by size and number, the huge demand for electricity from the many different consumers could only be met by supplying AC. Batteries then were moved out of the focus of attention for some time - but only relatively shortly. The early development of mobile devices such as a car or an electric bike gave rise to the need for mobile sources of electric energy, which quite obviously only batteries could provide and with some success. The first cars driven with electric motors enjoyed wider commercialization, unlike the first vehicle driven by a steam engine in Paris in 1769. The first electric car has been reported to be built by a Scottish inventor Robert Anderson approximately between 1832 and 1839, later known as a carriage. Not much is known beyond reports of the first experiments in 1837, and because rechargeable batteries had not yet been invented, his creation moved into oblivion. Professor Stratingh and his assistant Christopher Becker (Groningen, Holland) and the blacksmith Thomas Davenport (Brandon, Vermont) built small electric cars in 1835. Using the slowly improving (but still not rechargeable) batteries, Davenport and Robert Davidson built around 1842 slightly more practical and successful electric vehicles. An electrically powered tricycle built by Gustave Trouvé premiered once again in Paris in 1881 with a reported speed of 12 km h⁻¹. Serial production of electric cars started in 1890; William Morrison produced carriages with an electric motor of about 2.5 hp. In 1899 a car constructed by Camille Jenatzy aptly named Ne Jamais Contente (The never satisfied one) already passed the 100 km·h⁻¹ benchmark with a maximum speed of 105.8 km h⁻¹; the postal service in Germany operated the first electric transport vehicles. At an exhibition in Berlin, Germany, in 1899, the vehicle named "Electra" (Figure 1.1) operating with a $zinc/PbO_2$ battery was presented.

Around 1903 in large cities such as Paris, London, and New York, vehicular fleets comprised about at least one-third electrically driven vehicles, one-third steam driven, and less than one-third vehicles with internal combustion engines. F. Porsche, later famous for his sports cars and other developments, mounted two electric motors of 2.5 hp each into a carriage for the manufacturer L. Lohner – this Lohner–Porsche is sometimes considered as the first electric car. To charge the battery, Porsche added a small internal combustion engine.¹ In 1919 R. Slaby began building electric vehicles in Saxony, and later his company was acquired by J.S. Rasmussen, the proponent of AUDI. However, its lack of success resulted in the termination of its production in 1927. The car shown in Figure 1.2 weighs only

¹ Within this book, internal combustion engines are mostly motors working on the principles developed by Nikolaus Otto and Rudolf Diesel. Turbines may also be considered although they are less frequently used in mobile applications.



Figure 1.1 Battery-operated vehicle (Krüger, Berlin, Germany) of 1899.



Figure 1.2 Battery-operated car built by R. Slaby around 1919.

180 kg, and the 12 V battery provides 2 hp at the wheels, resulting in a top speed of 24 km $h^{-1}.$

In 1938 more than 2600 electric trucks were operated by German mail services, some of them lasted more than 40 years of service.

Somewhat in the shadow of the development of cars, battery-powered main line railcars were put into service by, e.g. railway companies in Germany in 1894.

The inventions of Otto and Diesel brought new developments (and German postal service put its last electric truck out of service in 1973). The rapid development of internal combustion engines, which were not inherently more powerful than electric motors (actually it was the other way round), but which did not need bulky, heavy batteries filled with etching liquids prone to crack and spill, quickly overwhelmed electric propulsion.

For a short period of time in history, everything seemed to be settled: Steam engines were suitable for heavy devices like locomotives, electrically driven cars were suitable for urban traffic, and cars with internal combustion engines were most suitable for the countryside because of their long range of operation. Further developments particularly in electrical engineering changed all these. The production of the magnetic ignition (Bosch, 1902) and of a reliable electric starter (Kettering, 1911) as well as the availability of cheap gasoline caused a steady decline of the electric car; thus the long journey of electric vehicles into some niches and oblivion elsewhere started.

Elsewhere the rapid development of the electric grid operated nation- or even continent-wide ensured a reliable supply of electricity up to the most remote villages – almost. As described in Chapter 2 in detail, devices for the storage of electric energy have always been used in remote places, and because electric energy can economically be stored only by converting it into chemical energy (and vice versa), energy conversion devices have always been associated with storage.

This is currently changing again, but slowly in some places and in dramatic steps. Several factors can be identified easily:

- Many energy conversion processes are based on the use of fossil fuels, which are limited in supply; in some cases, the end of its use is imminent (peak oil).
- The excessive use of fossil energies results in a substantial generation of carbon dioxide. Whether this is really a cause of climate change remains an open question for many. The prevailing advice is that we better not wait for the outcome of an experimental verification of this thesis as there might be only one try.
- Mobility causes not only congestions and traffic jams but also noise and air pollution. This again can be traced back to vehicles using internal combustion engines. Their replacement by other types of engines can possibly provide substantial relief.
- The use of other forms of energy like wind, photovoltaics, hydropower, or solar heat requires large storage devices for matching fluctuating supply and demand,²

² Load leveling (LL) means matching supply and demand in the long run: between day and night, winter and summer, and beyond. Power quality (PQ) (management) means keeping as constant as possible major electric characteristics like voltage or frequency. Peak shaving (PS) means compensating sudden changes in supply and demand (when e.g. several major consumer are switched on resulting in a drop of grid voltage and frequency without PS).



Figure 1.3 Actual power delivery from a wind farm (76 turbines) in Chap-Chat, Quebec, Canada, on 16 March 2004.

peak shaving, and power quality management. Most of the renewable sources are coupled to the grid by DC intermediates, thus cannot be used for frequency stabilization. To maintain grid frequency at ± 0.1 Hz in e.g. Germany, 2.7 GW power from sources AC-coupled to the grid are needed for regulation within one half of a sine wave, i.e. within less than 10 ms.

More extensive realization of these demands will be possible only when further stationary and mobile energy storage and conversion devices become available. Typical changes of power provided by windmills are shown in Figure 1.3 for a wind farm in Cap-Chat (Quebec, Canada) with 76 turbines on 16 March 2004.

Current reports on power outages as listed in Figure 1.4 (next page) provide only some relief. The previous figures illustrate only details and consequences of a fast moving trend: changes in the contributions from various primary energy sources to electricity production. The distribution of electricity in 1973 is shown in Figure 1.5 (next page). A few decades later (Figure 1.6, next page), this had changed significantly. Finally the change has become even more visible – with "other" including all renewables (Figure 1.7, next page).

With a constantly growing fraction of electric energy generated from renewables, storage becomes ever more important, in particular when their contribution is as large as 29% in Germany in 2015 (with 12.3% from wind and 6% from photovoltaics, two particularly volatile sources).





Storage of electric energy is possible in various ways. Mechanical:

- Pump storage power plants
- Compressed air storage power plants (CAES, compressed air (or gas) energy storage)
- Flywheels



Electrical:

- Capacitors
- Coils

Electrochemical:

- Accumulators
- · Flow batteries
- · Electrolyzers and regenerative fuel cells

Pumped storage systems utilize the potential energy of water stored at a higher level in a natural or artificial lake. Upon utilization this water propels turbines, thus converting this energy into electric energy collected in a lower lake. When there is a surplus of electric energy in the grid, water is pumped back into the upper lake either by the turbines or by separate pumps. In 2011, Germany had 33 power plants with a total power generation capacity of 6.6 GW; only one additional plant is scheduled to become operational in 2024. This apparent lack is because plants can be constructed at reasonable costs only at locations where both lakes are either present or created easily with a sufficiently large difference in elevation. The technology is reliable and provides high efficiency: About 75–85% of the stored energy can be retrieved. Because only evaporation of water causes losses, these plants have

excellent long-time storage properties, making them highly attractive for seasonal energy storage. Plants can be switched on and off within approximately 15 seconds without using external energy sources (blackstart capability); thus they can be used for short-term storage (daily load leveling) as well. Reports indicate that as of 2017 more than 90% of worldwide storage capacity for electric energy was pumped hydro.

In CAES surplus electric energy from the grid is used to pressurize air (typically to approximately 10 MPa), which is subsequently stored underground in large cavities. Upon discharge the pressurized air is fed into a gas turbine connected to an electric generator (down to a pressure of typically 7.5 MPa). The pressurized air saves the energy otherwise consumed to pressurize air needed for the combustion process in the turbine. Worldwide there are only two plants in operation, one in the United States and the other one in Germany. There are two modes of operation: In the diabatic mode the heat generated during is not utilized, resulting in an overall efficiency of 45%. When this heat is recovered, the system is operating in the adiabatic mode at 55% efficiency. The plant operating in Huntorf, Germany, can supply 290 MW into the grid; during charging, up to 60 MW is drawn from the grid. A suitably large underground reservoir is needed; in this example, it is an exhausted cavity from salt mining with 300 000 m³. Availability of such cavities of sufficient size and stability is required for building this kind of storage plant. Small-scale versions of this setup (SSCAES, small-scale compressed air (or gas) energy storage) have been developed, where the compressed air is stored in cylinders at pressures up to 300 bar. Overall efficiency is about 50%, and lifetime is limited by mechanical fatigue of the cylinders.

Another somewhat complicated process related to the previous one utilizes off-peak electricity for compressing cleaned ambient air. When cooled sufficiently, the air is finally liquefied and stored in insulated tanks at approximately -196 °C. Energy is retrieved by pumping the liquefied air into a pressurized container. By applying waste heat, the liquid is evaporated, yielding gas at high pressure. This pressurized air is used to assist in operating a gas turbine as in the previous example.

Flywheels can be coupled directly to electric drives operating in the discharge mode as generators. Known applications are of limited size, e.g. in a sports car a flywheel powers two electric motors at the front wheels during short periods (six to eight seconds) of acceleration with 160 additional horsepowers. The flywheel is charged upon braking up to 40 000 rotation per minute. Larger devices have been employed in buses (gyrobus) where recharging is performed at bus stops. The challenges to mechanical engineering are substantial, and widespread and large-scale application appears to be unlikely.

Direct, i.e. without conversion into other forms, storage of electrical energy can be achieved using coils and capacitors. Huge magnets containing superconducting wires as employed in particle detectors at research facilities like CERN, Geneva, store indeed substantial amounts of energy. The magnet at the hydrogen bubble chamber stores 216 kWh at a current of 5700 A and a self-inductance of 48 Hy at a weight of 276 ton. Tentative estimates for large storage projects (5000–10 000 MWh) suggest large coils (several 100 m in diameter), which cause huge magnetic field requiring remote or underground installation. Apparently this mode of storage is not very realistic on a large scale. On a small scale, superconducting magnetic energy storage may be a local short-term storage solution.

Conventional capacitors as employed everywhere in electronics and electric engineering have not been employed until recently for storing substantial amounts of electric energy because of insufficient capacity and substantial self-discharge. New applications for improved capacitors and new applications especially with electric motors, which can be easily used as generators, also have changed the situation dramatically, resulting in the successful development and application of supercapacitors.

In all electrochemical storage and conversion systems, electric energy is converted into chemical energy (charging the battery) and back upon discharge. Again this is no direct storage without conversion as conversion losses are to be expected. Traditionally electrochemical energy storage systems have been associated with a few major fields of application:

- Uninterruptible power supply for e.g. hospitals, traffic supervision and control, and aircrafts.
- Starting, lighting, and ignition (SLI) in vehicles.
- Power supply at places off the grid (remote area power supply [RAPS]).
- Mobile and portable³ applications in cameras, mobile phones, electronic gadgets, mobile computers, etc.

More recently the need for storage systems matching the variable supply of electricity from renewable energy sources has been added as a major application and challenge. Because this field of application may become a major challenge, targets for this grid-related application are of general interest. The data in Table 1.1 pertain mostly to the US market.

Attempts at improved energy efficiency and higher utilization (this is sometimes the most effective way at avoiding the need for more power plants) require more powerful storage systems for e.g. energy recuperation in transportation. Recuperation successfully employed with electric railways operating with overhead wiring is not feasible with all kinds of electric supplies (AC or DC). In addition it is limited in terms of power intake of the system when many locomotives are breaking. In subway systems or with other forms of urban mass-transit systems, other energy storage devices handling huge excess power from many cars breaking at the same time are required. Again electrochemical systems appear to be the most promising solution.

Matching systems to conceivable applications is visualized in Figure 1.8.

A term closely related to the figure above is "operating reserve." It names the amount of electric energy storage and conversion available on various timescales for receiving excess or supplying needed extra energy. Based on the response time (see Figure 1.9), various operating reserves are considered

³ The distinction is not firmly defined, presumably a car is mobile but not portable, whereas a camera is mostly portable. A mobile phone is both – thus adding to the confusion. Presumably small storage devices should be associated with portable, large ones with mobile (except the cell phone).

Application	Duration	Purpose	Targets
Frequency and area regulation	Short	Matching supply and demand locally (power quality)	Service cost: US\$20/MW Roundtrip efficiency: 85–90% System lifetime: 10 yr Discharge duration: 0.25–2 h Response time: ms
Integration of renewables	Short	Compensating short term fluctuations of photovoltaics energy delivery	Roundtrip efficiency: 90% System lifetime: 10 yr Capacity: 1–20 MW Response time: s
Deferral of grid upgrade	Short	Delays or avoids investments in transmission and distribution	Cost: US\$500/kWh Capacity: 1–100 MW Reliability: 99.9% System lifetime: 10 yr
Load following	Long	Enables operation of energy conversion systems with constant high efficiency at all loads	Capital cost: US\$1500/kW or US\$500/kWh Running cost: US\$500/kWh Discharge duration: 2–6 h
Matching daily demand fluctuations	Long	Storage of excess energy during time of high supply, delivery during high demand (load leveling)	Capital cost: US\$1500/kW or US\$500/kWh Running cost: US\$250–500/kWh Discharge duration: 2–6 h Efficiency: 70–80% Response time: 5–30 min
Matching seasonal demand changes	Very long	Storage of excess energy during time of high supply, delivery during high demand (wind, photovoltaics)	1

 Table 1.1
 Development and performance targets for grid-related storage.



Figure 1.8 Typical discharge times and rated powers of electrochemical storage systems. For acronyms, see text.



(the time windows are subject to national as well as international regulation and may vary; this also applies to the times of notification, deadline for offers, etc.):

- Primary operating reserve: The committed amount of energy must be supplied within 30 seconds after requesting it.
- Secondary operating reserve: The same within a time frame of 5 minutes.
- Tertiary operating reserve: The same within a time frame of 15 minutes.

In addition, a so-called "spinning reserve" may be considered. It is the extra amount of electric energy, which can be obtained from an electric generator by increasing its power output. The "non-spinning" or supplemental reserves can be classified as given above. Beyond these reserves, supply from other power stations is expected. Quite obviously electrochemical systems are the most suitable ones.

In a typical installation brought online in August 2017 in Germany, a total energy of 15.9 MWh can be stored. It comprises 4008 lithium-ion battery modules providing up to 14 MW of power, equivalent to 1% of primary operating reserve in Germany.

Given the capability of a water electrolyzer (for details, see Chapter 9) to operate safely at a fraction of its nominal capacity (down to less than 10%) and at significant overload (up to 300%), an electrolyzer may also provide an operating reserve in a different way by reducing its energy uptake in times of need for energy elsewhere.

A comparison in Table 1.2 of energy storage systems, although data may change almost daily, and thus the list provides only a passing snapshot, lists many arguments discussed above.

Some systems are omnipresent (++) at various scales (lithium ion mostly in portable/mobile devices, lead-acid as starter battery and in uninterrupted power supply devices, supercaps as short-term storage in many electronic devices, pumped hydro in grid storage at those few places where topography permits), some are basically available, but not very widespread applied for various reasons (+), flywheel devices and thermal storage are still expensive, suitable locations for compressed air are even rarer than those for pumped hydro, Na-S is still expensive, flow batteries are still considered "experimental," and some are unlikely for practical use (Table 1.2). Certainly the table is all but final, and definitely many

Туре	Power	Mobile	Discharge time (h)	Response	Efficiency (%)	Cycle life at 80% DOD ^{a)}	Com- mercial?	Cost (US\$/kWh)
Pumped hydro	MW-GW	-	>8	Fast	70-85	$2-5 \times 10^{4}$	++	_
Electromagnet	MW	-	0.25	Fast	90–95	0.11×10^4	?	_
Compressed air	MW-GW	-	0.1-15	Very fast	60-79	$0.9 - 3 \times 10^4$	+	-390 to 430
Flywheel	kW	+	0.1–1	Fast	>90	$> 2 \times 10^4$	+	_
Supercap	kW	+	0.02–1	Very fast	>95	110×10^4	++	_
Thermal	MW	-	1–45	Slow	60	$0.4 - 1 \times 10^4$	+	_
Lead-acid	kW-MW	++	0.1-4	Fast	70-76	200-1500	++	625-1150
Na-S	MW	-	1–10	Fast	85-90	210-4500	+	445-555
Li-ion	kW-MW	++	0.1–1	Fast	>90	$5 - 7 \times 10^{3}$	++	900-1700
Flow battery	kW-MW	-	1-20	Fast	75-85	$0.5 - 14 \times 10^4$	+	340-1350

Table 1.2Comparison of some energy storage systems for e.g. utility transmission anddistributed grid support.

a) DOD, depth of discharge.

numbers and judgments from the author's point of view, thus subject to further discussion and development. Nevertheless electrochemical systems predominantly cover a wide range in terms of both power and energy capacity; many of them can easily be scaled from very small to very large, and they all share one major advantage: They store and release electric energy, the most versatile and generally most "valuable" form of energy. Together with the growing fraction of energy generated using renewable sources, which offer supply only depending on the time of day, season of year, or strength of wind, they offer a valuable or perhaps even pivotal complement in the future of energy derived from fossil and nuclear sources. Finally most electrochemical systems can be placed almost everywhere because of their low environmental impact (no fumes, no smoke, low excess heat generation, no need for bulky fuel supply, almost no noise), which is particularly attractive because it minimizes transmission losses and may help in moving to less centralized infrastructure with all associated risks and inefficiencies. Mostly they have short response times, thus meeting demands from electricity consumers requiring high reliability of electricity supply at very constant voltage and frequency and matching the volatility of renewable power supplies with e.g. sudden changes of power generated in a photovoltaic plant with sudden clouding of the sky (for a comparison, see Figure 1.10).

In consideration of energy storage and conversion systems for present and in particular for future systems and economies, the "sustainability profile" of systems and resources should be taken into account (see Table 1.3).

Critical properties of all energy storage systems are gravimetric and volumetric energy and power densities. Although actual numbers may vary slightly because of different assumptions regarding chemical reactions proceeding during conversion and inclusion (or exclusion) of reactants, Table 1.4 provides an overview of the density as the property connecting volumetric and gravimetric data.



Figure 1.10 Storage capacity and typical discharge times of various storage technologies.

Table 1.3Sustainability profiles of selected processes relevant in energy conversion and
storage.

Sustainability profile						
Technology	Lasts a long time	Does no harm	Leaves no change	Needed breakthroughs		
Solar	+	+	+	Cheaper and more efficient cells, electricity storage		
Wind	+	+	+	Electricity storage		
CO ₂ sequestration	0	+ Leaks?	_	Fundamental understanding of reactions		
Nuclear	0	+ Radioactivity	_	Waste disposal, materials for fusion reactors		
Biofuels	+	+	+	Improved utilization of cellulosis, chemical catalysis		
Electromobility	+	+	+	Better batteries, clean sources of electric energy		

The present state of things as listed above can be summed up visually in Figure 1.11.

Further and more specific numerical values – still theoretical ones – are collected in Figure. 1.12 on selected systems again.

Batteries of every kind are obviously not competitive enough, and practical values are significantly lower (generally about 25% of the theoretical value for rechargeable system, up to 50% for primary systems) as discussed in Chapter 3. Putting things into a practical perspective yields a plot (Figure 1.13) of driving range given a single filling of the tank in a car; it may be a 50 l gasoline tank or a 350 kg battery.

Again, the data that are only snapshots of current possibilities and may change almost daily illustrate disappointingly the capabilities of basically every electrochemical storage system. Using a fuel cell running on gasoline or a simple organic fuel may be a much more effective option as discussed in Chapter 9.

Sometimes hydrogen is considered as an energy carrier alternative to electricity. When comparing hydrogen or hydrogen-containing chemicals (e.g. toluene/methylcyclohexane⁴ or dimethylether⁵), typical advantages and disadvantages are easily identified (see Table 1.5).

⁴ Toluene + 2.5 H₂ \rightarrow methylcyclohexane can be considered as the storage reaction, the reverse process is the release of hydrogen, and the participating liquids may be considered as storage media.

⁵ Dimethylether (DME) is a carrier with properties (in technological terms) similar to diesel fuel. Hydrogen can be released from DME in catalytic processes. As a fuel replacement, it also can simply be burned with less emissions.

	Volumetric energy density		Density	Gravimetric energy density	
	kWh l ⁻¹	MJ l ⁻¹	kg l ⁻¹	kWh kg ⁻¹	MJ kg ⁻¹
Gasoline	8.6	31.0	0.7	12.2	44.0
Gasoline high octane	8.4	30.3	0.7	12.0	43.2
Diesel fuel	9.6	35.0	0.8	11.8	42.7
Methanol	4.4	16.1	0.792	5.5	19.9
Bioethanol	5.9	21.2	0.8	7.4	26.6
Plant oil	9.2	33.1	0.9	10.2	36.8
Biodiesel	8.9	32.0	0.8	10.3	37.0
Synthetic gasoline	8-10	30-35	0.8-0.9	10-12	38-44
Autogas	6.4	23.0	0.5	12.8	46.1
Methane	5.9	21.5	0.000656 ^{a)}	13.9	50.3
Propane	7.5	27.3	0.000493 ^{a)}	12.9	46.7
Butane	7.6	27.7	0.00248 ^{a)}	12.7	46.0
Compressed natural gas at 200 bar	11.5	41.4	0.7	14.4	52.0
Hydrogen, liquid, $T = -253 ^{\circ}\text{C}$	2.3	8.3	0.07	33.3	119.9
Hydrogen 200 bar	0.5	1.8	0.02	33.3	119.9
Hydrogen 650 bar	1.3	4.5	0.04	33.3	119.9
Lead–acid accumulator	0.05	0.2	1.1	0.06	0.22
Lithium-ion accumulator	0.5	1.8	0.4	0.2	0.72
Hard coal	8.8	31.7	1.1	8.1	29.3
Wood pellets	3.1	11.2	0.7	4.8	17.3

Table 1.4Volumetric and gravimetric energy densities of selected energy storage
materials.

a) In gas state.



Figure 1.11 Gravimetric and volumetric energy densities of common storage materials preferably for mobile applications.



Figure 1.12 Theoretical gravimetric and volumetric energy densities of selected rechargeable batteries with selected fuels for comparison.



Figure 1.13 Driving ranges of a car running on different energy storage systems; ICE, internal combustion engine.

It is beyond the scope of the present book to deal with this subject, sometimes called "hydrogen economy," but a short look in Table 1.6 at hydrogen in the framework of storage of electric energy based on electrolysis of water with surplus electric energy from wind and photovoltaics is instructive.

Options of hydrogen generation and utilization are schematically assembled in Figure 1.14.

Carrier	Operation	Transmission
Electricity	Easy	Simple, but losses growing with distance
Chemicals	Need for conversion	Only transportation costs, no losses

 Table 1.5
 Advantages and disadvantages of energy carriers.

Table 1.6 Use of hydrogen in energy storage and distribution concepts.

System	Conversion into electric energy by	Efficiency (%)
Feeding H_2 into the natural gas distribution network	Gas turbine Gas and heat power station	27.4 33.9
Methane production	Gas turbine Gas and heat power station	17.9 28.1
Liquid organic hydrogen carrier	Gas motor Fuel cell	29.0 30.4



Figure 1.14 Options of hydrogen generation and utilization.

Although energy storage by water electrolysis is certainly a valid storage option, which would gain attention in case of hydrogen/dioxygen fuel cells, it is generally not considered explicitly within a book like the present one, except when discussing particular types of fuel cells that can also operate as an electrolyzer; for details, see Chapter 9.

With a still growing market penetration of both established and new systems, features and properties of secondary batteries may become even more relevant for users. The relative importance of some features for selected typical applications is listed in Table 1.7; this ranking is certainly only one of presumably several possibilities.

Relative importance	Mobile/portable application	Electric vehicle	Grid
Highest	Energy density	Power density	Cost
	Safety Cost	Safety Lifecycle cost	Size Power/energy density
Lowest	Power	Energy density	Safety

Table 1.7 Relative importance of system properties for selected applications.

When attempting to match currently available (or at least sufficiently developed) storage technologies with typical applications besides the ubiquitous mobile and portable ones, four categories of application can be defined:

- 1) Remotely used low-power application in broadcasting, supervision, emergency communication, autonomous operation at 10–30 days, power range from 1 Wh to 100 kWh, typical charge current of $0.05 \cdot C_{10}$,⁶ typical discharge current < $0.01 \cdot C_{10}$, converted capacity per cycle at 5%, typical number of full cycle equivalents per year at 20, charged from photovoltaics.
- 2) Remote medium-power application in isolated locations for houses, small settlements, autonomous operation at 1–10 days, power range from 10 Wh to 1 MWh, typical charge current $0.05-0.2 \cdot C_{10}$, typical discharge current of $0.02-0.1 \cdot C_{10}$, converted capacity per cycle at 10–30%, typical number of full cycle equivalents per year at 50–400, charged from photovoltaics.
- 3) Network-connected application with peak leveling (e.g. with wind turbines), autonomous operation 0.25-10 hours, power range from 10 kWh to 1 MWh, typical charge current of $0.2-0.5 \cdot C_{10}$, typical discharge current $0.25-0.5 \cdot C_{10}$, C_{10} , converted capacity per cycle at 50–80%, typical number of full cycle equivalents per year at 300–1000, charged from photovoltaics or wind energy.
- 4) Power-quality management, autonomous operation at 2–600 seconds, power range from 1 Wh to 1 MWh, typical charge current of 100 ⋅C₁₀, typical discharge current of 100 ⋅C₁₀, converted capacity per cycle at 50–80%, typical number of full cycle equivalents per year at 3000–100 000.

Nine selected storage technologies turn out to be more or less suitable for a given application:

- Lead-acid battery
- Supercapacitors
- Compressed air storage
- Lithium-ion batteries

⁶ C_{10} : Maximum amount of energy from a unit when discharged in 10 hours.

- Flywheels
- Nickel-cadmium batteries
- Redox flow batteries

Results of matching application and technology are shown in Figure 1.15.

With respect to particular applications, Figure 1.16 shows a more detailed illustration of grid applications.

Depending on further technological and economic development shifts and changes, this will also happen when external factors like legal or political changes come into play.

A criterion of varying importance is price, in particular price per kilowatt-hour. For example, a kilowatt-hour of electric energy costs about $\notin 0.20$ (in Europe in 2010), while 1 kWh obtained from an alkaline battery (size AA) costs about $\notin 60$ (one will need about 300 of these cells). With a AAA cell, this price will double because these cells cost about the same as AA cells at a much lower energy content. During the production of a cell 40 to 500 times the energy later made available by the device is consumed. Thus, in terms of energy and economics, primary (non-rechargeable) batteries are rather inattractive in particular for continuous or at least frequent high-load applications. Other arguments are in many cases quite apparently more important: The distance to a power outlet combined with low energy consumption of a device, e.g. an electronic clock or monitoring instrument. Even the use of rechargeable batteries with a substantially better economic and ecological balance may be not justified because of higher initial costs (secondary battery plus charger), higher self-discharge of a possible secondary system, and associated costs of more frequent replacements/recharging.



Figure 1.15 Performance index (in % with a higher percentage implying better suitability) for nine systems in four categories.



Figure 1.16 Gravimetric power and energy densities of secondary electrochemical storage and conversion systems currently investigated for grid applications.

Finally a realistic assessment of efficiencies and related release of CO₂ in transportation may help to put some options in perspective. The sometimes rather unlimited enthusiasm connected to the more widespread use of electric vehicles does not match reality. At first glance a fume-squelching diesel engine propelled railway locomotive may seem as a poor option when compared with its electric counterpart operated from an overhead wire. When looking at the overall energy efficiency, comparing the amount of fuel consumed for movement of a load using the diesel engine and using the electric locomotive fed with electric energy generated in a thermal power plant, taking into account losses during transmission of the electric energy, the electric locomotive suddenly becomes a very poor option. Air pollution from the diesel engine may be worse, but overall energy efficiency is better. In addition, costs are higher for the electrically powered because of much higher investments. Both energy efficiencies and emissions can be shown in a careful wheel-to-wheel analysis, thereby revealing that the arguments turn out to be more complicated than initially assumed. In case of the electric locomotive, these transformation steps must be considered from a thermal power plant: $coal/gas \rightarrow steam$ turbine \rightarrow generator \rightarrow transformer \rightarrow transmission \rightarrow transformator \rightarrow electric motor. Finally the overall efficiency is the mathematical product of the efficiencies of the steps. In the case of the diesel locomotive, the sequence is shorter: diesel fuel \rightarrow diesel engine \rightarrow wheel. In the end higher efficiency means less fuel is needed and less carbon dioxide is emitted. Certainly the situation changes when renewable energy sources provide the electric energy. Furthermore even minor details such as reported losses of 10-30% along the charging cable may be noteworthy.