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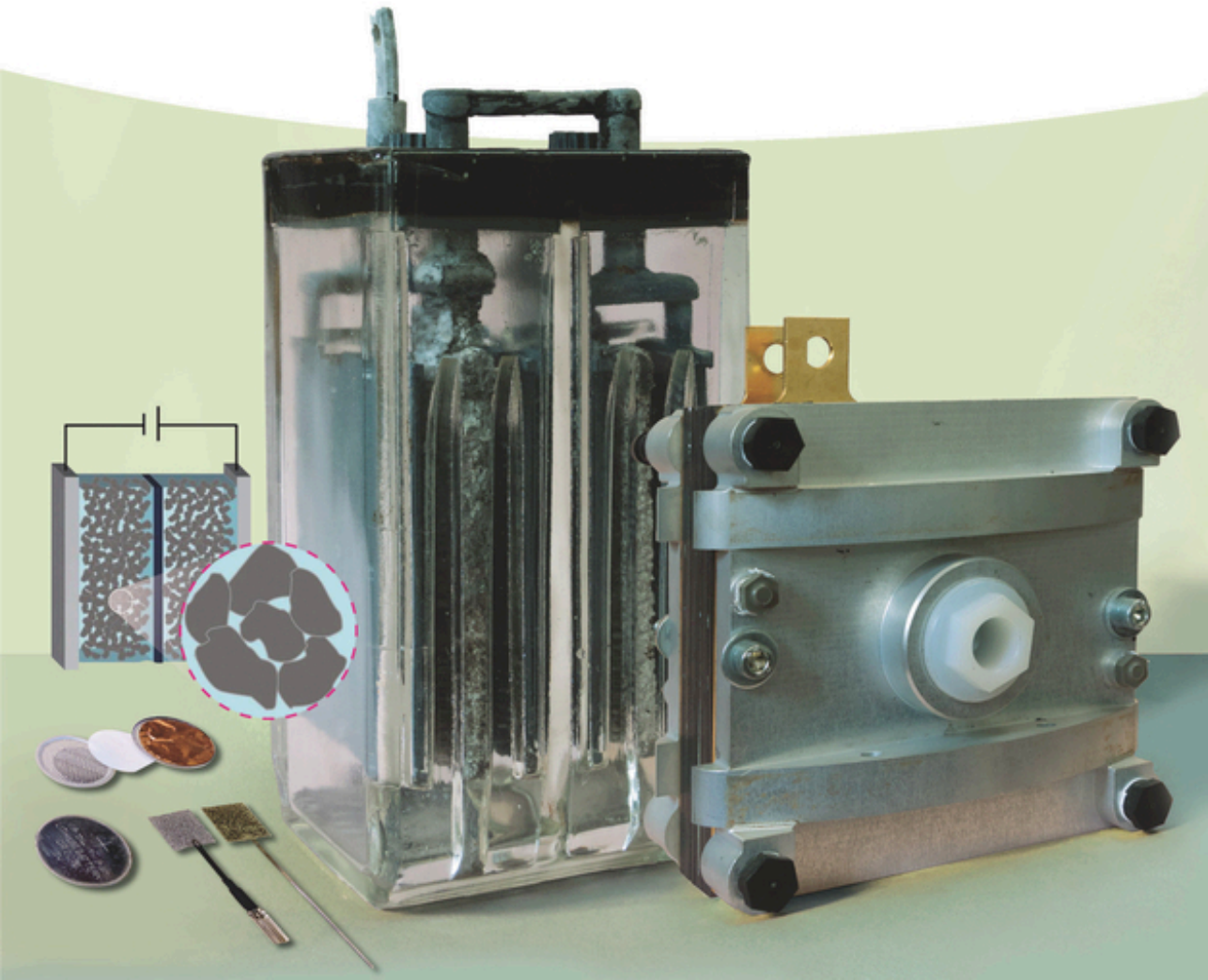
Rudolf Holze and Yuping Wu

Electrochemical Energy Conversion and Storage

An Introduction



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Yuping Wu and Rudolf Holze

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Foreword

We experienced in last years throughout of our planet, hard events, including extreme temperature changes, floods, wide burns of forests, and droughts, all related to climate changes, resulting from a continuous global warming during recent years. The global warming, from which we suffer, seems to result from greenhouse effects, connected to a monotonic growth of the concentration of CO_2 in our atmosphere. These bad changes in our living conditions on earth may result from the way we convert energy, using fossil fuels in power stations, industries, and propulsion, which combustion evolves continuously CO_2 that accumulates in the atmosphere, absorbs sun radiation, and bringing our planet to new physical equilibria at increasing temperatures. On top of that, the way we convert today energy to electricity and propulsion leads to unbearable levels of pollution in most populated urban parts of the world.

These situations should force the world population in all countries to change the way they convert energy in producing electricity and maintaining effective transportation. An obvious reaction to these global challenges is to move from fossil fuels to sustainable, renewable, and "green" energy sources, changing propulsion by burning fuels in internal combustion engines to electro-mobility by electric vehicles. Harvesting solar energy by photovoltaic cells in panels may provide all the energy needs of the world human society at any visible future. Fortunately, there is a great success during recent years to develop more and more effective photovoltaic (silicon-based) solar panels, which become cheaper and cheaper. The biggest challenges in changing our energy economy toward a better sustainability, low pollution, and stabilized climate are the needs for effective technologies of large energy storage (in terms of thousands of terawatt-hours, globally) and for electro-mobility.

It is generally understood and accepted that modern electrochemistry has the capability and potential to meet these great challenges, via development of advanced electrochemical power sources and energy storage devices, including rechargeable batteries, super-capacitors, water electrolysis cells for hydrogen production and fuel cells. Consequently, we see in recent years worldwide efforts to develop electrochemical energy technologies. The communities working on these challenges increase, and new electrochemistry groups are established in many leading universities throughout the world. The many newcomers who join the

electrochemical energy community on a yearly matter obviously need effective and comprehensive guidance for their work. Thereby, the new book entitled "Electrochemical Energy Conversion and Storage" composed by Professors Y. Wu and R. Holze is coming in these days right on time. As explained further, this is a very comprehensive and educational book, which provides an integral view of all aspects related to electrochemical power sources, from the very basic roots to most practical aspects of this broad and complex field. The authors, Professors Holze and Wu, are distinguished scientists in the broad field of electrochemical power sources. They have collaborated for many years and have gained experience of decades, working on a wide scope of topics related to energy storage and conversion: batteries, fuel cells, relevant materials chemistry and engineering, analytical tools and related basic science. The book reflects very well their experience and long-term collaboration.

It raises some historical aspects at the beginning and starts actually with an important basic scientific background. It reviews in fact most important battery systems, primary, secondary, and flow systems. It reviews briefly important aspects of fuel cells and super-capacitors. Practical aspects are well incorporated in the description of the various devices. The depth of details in which the various devices are described provides the basic information required to understand operation and suitable usage, yet the level of information is not too excessive, meeting the main goal of the book to overview the very broad field of electrochemical energy storage and conversion technologies.

As explained above, this book will help many young scientists and newcomers to enter this field and to obtain an integrated view of it.

August 2021

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Preface

Extensive use of electric energy (or more commonly, electricity) is sometimes considered as an indicator of the advanced state of development of an industrialized society. This electric energy is produced by conversion of other forms of energy (it is not generated at all), most likely by burning fossil fuels and by employing nuclear chain reactions and utilizing the released heat in subsequent thermal conversion steps or by converting the kinetic energy of water flowing in a river to drive an electric generator. Already in an early stage of development, the need for storage of electrical energy to be used in mobile and portable devices has been realized: The first cars driven with electric motors. The rapidly growing number of sensitive applications depending crucially on an uninterrupted supply (e.g. in hospitals, traffic control, computers) has created demand for storage systems working even when the grid and the external supply have been interrupted. Finally the need for advanced modes of both conversion of electrical energy into other forms as well as from other forms into electrical energy combined with vastly enlarged systems for storage has grown dramatically with the growth of supply of energy from fluctuating sources (sometimes called renewable) like wind and photovoltaics.

Effective use of available options requires knowledge and information. This is apparent when looking at recently installed courses at universities or when looking at new fields of business explored by many companies. A textbook for students entering this field of energy technology, storage, and advanced energy utilization as well as for those already in the engineering field meeting new challenges has not been available for many years. The authors – both active in the field of electrochemical energy storage and conversion for quite some time – have prepared this book in an attempt to close this gap. It will be only a temporary relief because of the rapid changes and expansion of this field, but it may be at least a starting point.

Symbols and descriptions in figures are used according to suggestions by IUPAC (Pure Appl. Chem. **37** (1974) 499). When compared with older textbooks, this may occasionally result in minor confusion; the list of symbols, acronyms, and abbreviations will help (see Appendix). Frequently used terms and names are collected in a separate section, which will help readers not yet familiar with the language used in this field. Dimensions are separated by a slash (quantity calculus); square brackets are only used when necessary to avoid confusion. In reaction equations, solvent molecules that always form a solvation shell around ions in electrolyte solutions

are mentioned explicitly only when necessary to understand the phenomenon just discussed. Otherwise they are omitted for simplicity.

This book attempts in no way to provide a complete review or collection of publications related to electrochemical energy storage and conversion. References to publications are thus omitted.

Writing this book would have been impossible without help and support. Yuping Wu would like to take this opportunity to acknowledge the financial support of National Key R & D Program of China (2018YFB0104301), National Natural Science Foundation of China (No. 21374021 and 52073143), its Distinguished Youth Scientist Program (51425301) and Union Key Project (U1601214); R.H. was supported by the Fonds der Chemischen Industrie, which provided a generous grant covering many expenses related to preparing the manuscript. Parts of the manuscript were prepared during stays at Fudan University, Shanghai, and Nanjing Tech University, Nanjing: The generous hospitality of Yuping Wu, his group, and his universities and the stimulating environment as well as generous support from the Alexander von Humboldt-Foundation are gratefully acknowledged. Some installment was prepared when staying in the stimulating environment at the Université de Bourgogne enjoying numerous discussions with M. Vorotyntsev – generously supported by Deutsche Forschungsgemeinschaft. Finally discussions with A.K. Shukla at the Indian Institute of Science at Bangalore provided input; once again support by the Alexander von Humboldt-Foundation and a most generous host made this possible.

Of course all errors and omissions are exclusively the author's one – and they will thankfully accept hints and corrections.

February 2020

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Processes and Applications of Energy Conversion and Storage

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 $SmCo_5$ and $LaNi_5$ 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.

Electrochemical Energy Conversion and Storage, First Edition. Yuping Wu and Rudolf Holze.

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.

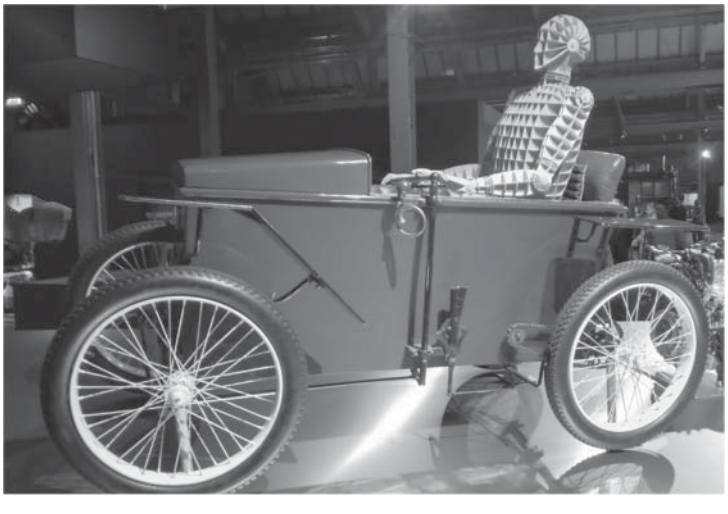

Figure 1.2 Battery-operated car built by R. Slaby around 1919.

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).

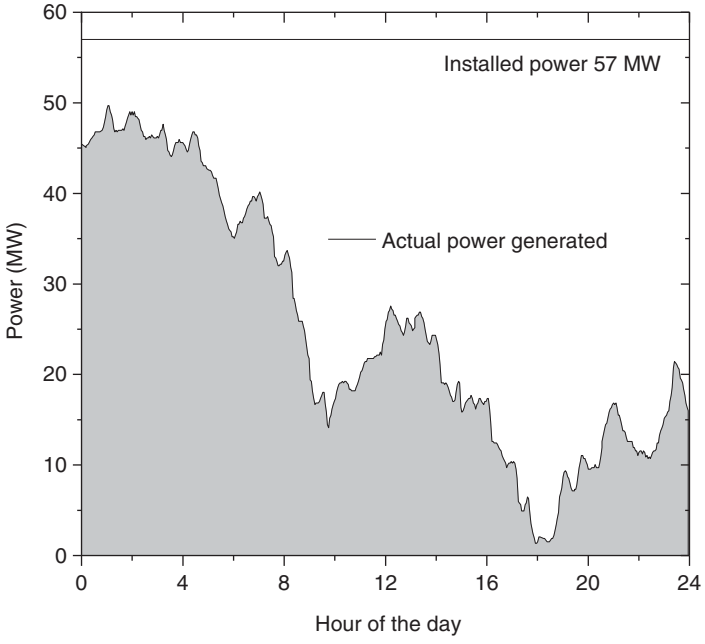

Figure 1.3 Actual power delivery from a wind farm (76 turbines) in Chap-Chat, Quebec, Canada, on 16 March 2004.

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).

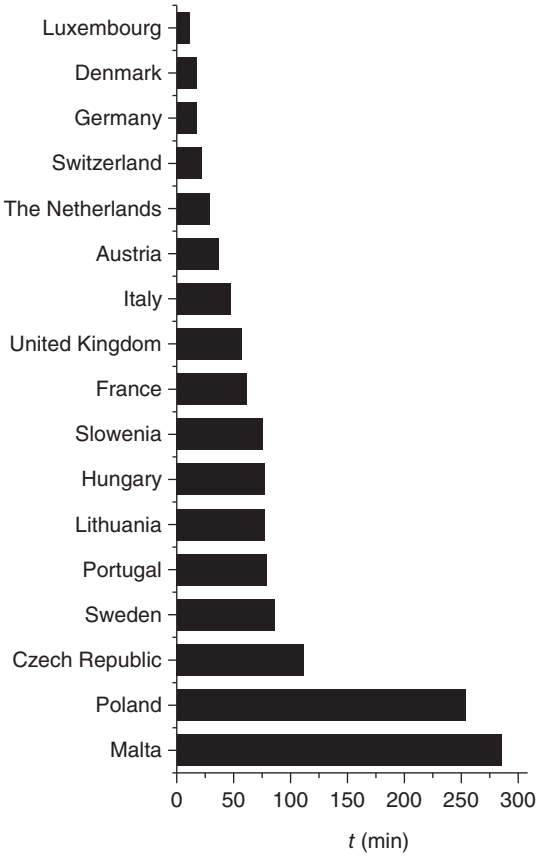

Figure 1.4 Power outages in minute(s) per year in 2013 in Europe.

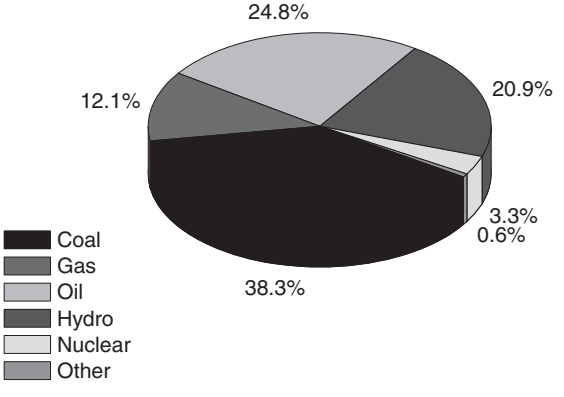

Figure 1.5 Primary energy sources in electric energy production 1973, total 6131 TWh.

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

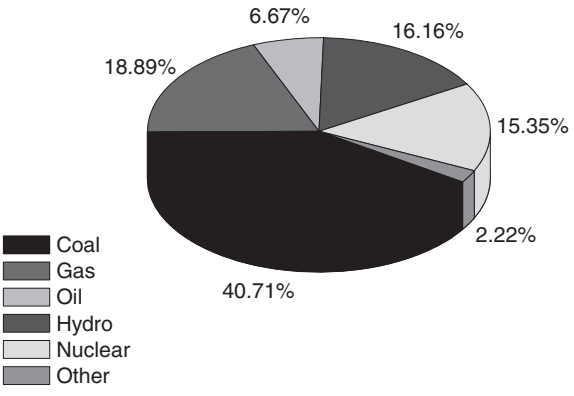

Figure 1.6 Primary energy sources in electric energy production in 2005.

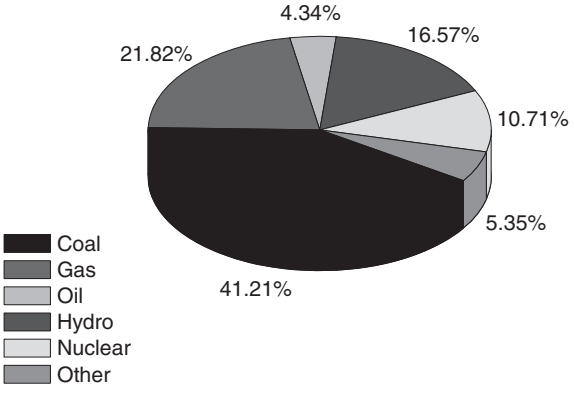

Figure 1.7 Primary energy sources in electric energy production in 2014, total: 23816 TWh.

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 m^3. 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 portable[3] 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).

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

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)	—

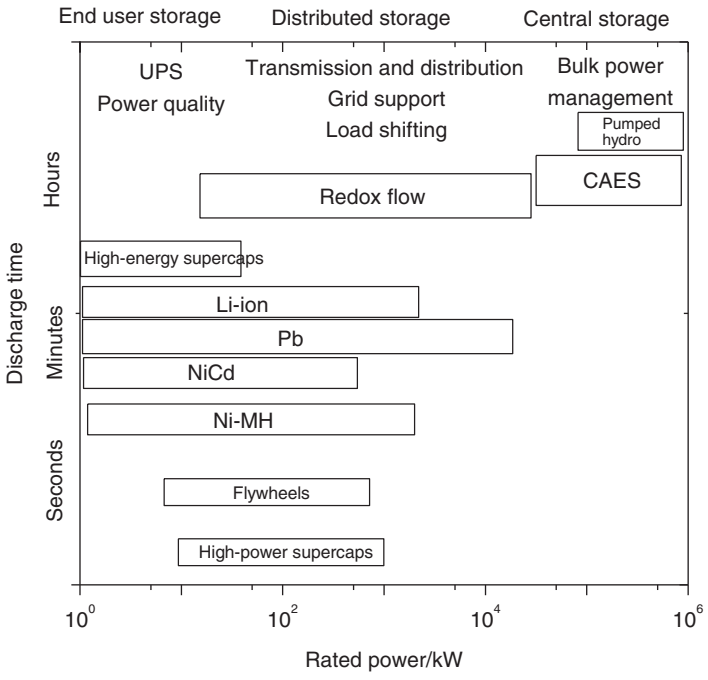

Figure 1.8 Typical discharge times and rated powers of electrochemical storage systems. For acronyms, see text.

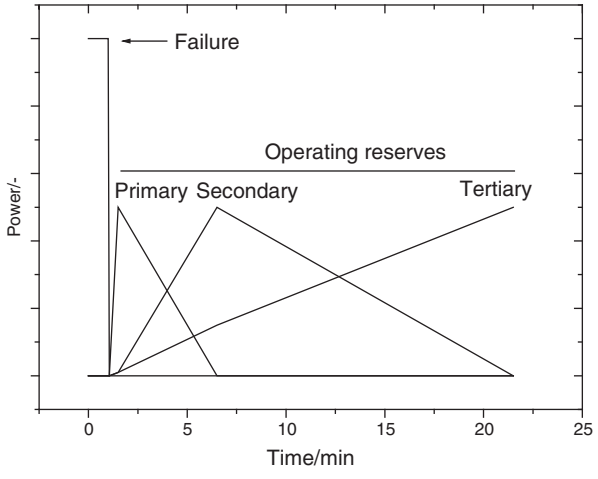

Figure 1.9 Schematic display of contributions from various operating reserves after failure of a power source.

(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

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

Type	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	$2–5\times10^4$	++	—
Electromagnet	MW	–	0.25	Fast	90–95	$0.1–1\times10^4$	?	—
Compressed air	MW–GW	–	0.1–15	Very fast	60–79	$0.9–3\times10^4$	+	−390 to 430
Flywheel	kW	+	0.1–1	Fast	>90	$>2\times10^4$	+	—
Supercap	kW	+	0.02–1	Very fast	>95	$1–10\times10^4$	++	—
Thermal	MW	–	1–45	Slow	60	$0.4–1\times10^4$	+	—
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	$5–7\times10^3$	++	900–1700
Flow battery	kW–MW	–	1–20	Fast	75–85	$0.5–14\times10^4$	+	340–1350

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.

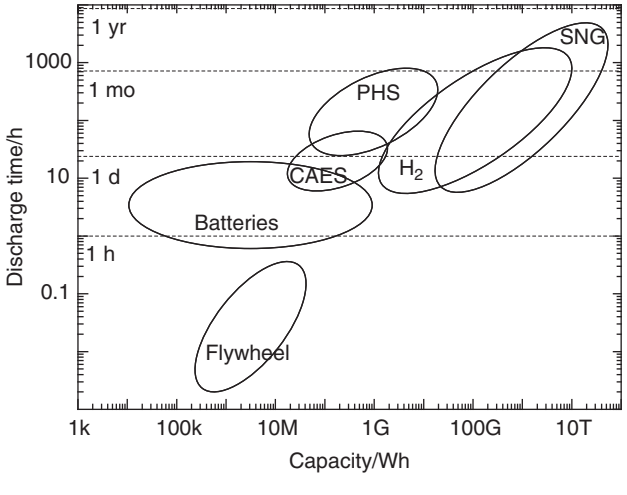

Figure 1.10 Storage capacity and typical discharge times of various storage technologies.

Table 1.3 Sustainability 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/methylcyclohexane[4] or dimethylether[5]), typical advantages and disadvantages are easily identified (see Table 1.5).

4 Toluene + 2.5 H_2 → 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.