

Energy Storage

Robert A. Huggins

Energy Storage

Fundamentals, Materials and Applications

Second Edition



Springer

Robert A. Huggins
Department of Materials Science
and Engineering
Stanford University
Stanford, CA, USA

ISBN 978-3-319-21238-8 ISBN 978-3-319-21239-5 (eBook)
DOI 10.1007/978-3-319-21239-5

Library of Congress Control Number: 2015945958

Springer Cham Heidelberg New York Dordrecht London
© Springer International Publishing Switzerland 2010, 2016

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media
(www.springer.com)

Preface

Introduction

Energy is necessary for a number of reasons; the most basic and obvious involve the preparation of food and the provision of heat in order to make life comfortable, or at least, bearable. Subsequently, a wide range of technological uses of energy have emerged and been developed, so that the availability of energy has become a central issue in society.

The easiest way to acquire useful energy is to simply find it in nature as wood or as a hydrocarbon fossil fuel. But it is advantageous to simply convert what is available in nature into more useful forms. The processing and conversion of raw materials, especially petrochemicals, has become a very large industry.

Wood

Wood has been used to provide heat for millennia. It can be acquired as needed by foraging or cutting. When it is abundant, there is relatively little need for it to be stored. However, many societies have found it desirable to collect more wood than is immediately needed during warm periods during the year, and to store it up for use in the winter, when the needs are greater, or its collection is not so convenient. One can still see this in some locations, such as the more remote communities in the Alps. One might think of this as the oldest and simplest example of energy storage.

It was discovered long ago that it is possible to heat wood under oxygen-poor conditions so that some of its volatile constituents are driven off, leaving a highly porous carbon-rich product called charcoal. Charcoal has a higher heating value per unit weight than the wood from which it was produced, approximately $30,400 \text{ kJkg}^{-1}$, instead of $14,700 \text{ kJkg}^{-1}$. Thus it is more efficient to store and to use

to produce heat. This is an example of the conversion of a simple fuel into one with a higher energy value before storage.

In the nineteenth century 84 % of the energy worldwide, roughly 10^{18} megajoules, or about 1 yottajoule (YJ) was supplied by wood, charcoal, and crop residues.

Coals

Natural deposits of carbon were also discovered long ago; it was found that they can likewise be readily burned to produce heat. These solid, carbon-rich materials are often described as various types of coal, with different energy contents. The lowest energy content form is called peat, followed by lignite (brown coal), sub-bituminous coal, and hard coal (or anthracite). Their approximate specific energy contents are shown in Fig. 1.

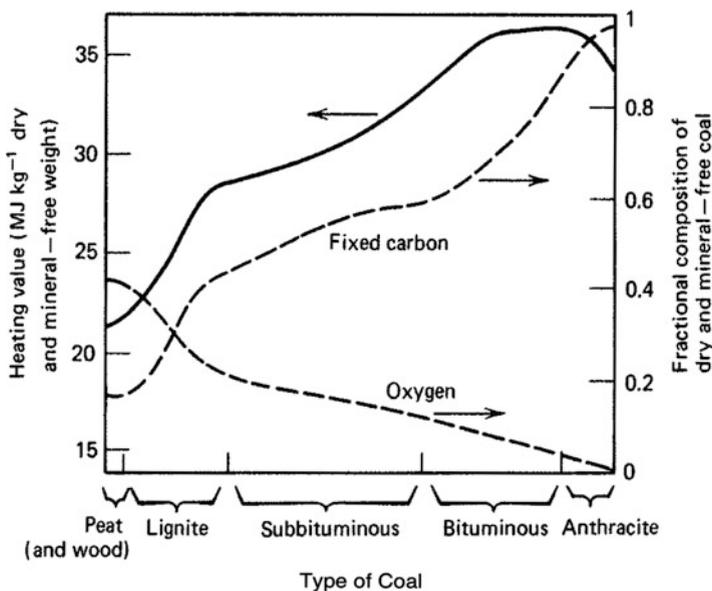


Fig. 1 Energy content and carbon, and oxygen contents of the different types of coal. Based on US DOE data

The harder forms have sufficient energy contents that it is economical to not only store them, but also transport them to other locations. Coals constitute the largest fossil fuel resource in the world, about 5.3 YJ, and are now the most important energy source in a number of places. Where it is available, coal is the least expensive fuel, less than oil or natural gas.

As in the case of wood, coals can be heated in an air-poor environment to produce a more valuable product, called coke. Coke can then be burned to produce more heat per unit weight and volume than the coal from which it was made, while also producing very little smoke. Because of its porosity, relatively high hardness, and higher energy content, coke is used in blast furnaces to reduce iron oxide to molten iron, an early step in the production of steel.

There is an increasing concern about the toxic contaminants that are originally contained as minor constituents in coals. Because of the concern about such particles getting into the atmosphere, they are often trapped in equipment that is designed to reduce air contamination from coal-burning power plants. They also appear in the coal ash, the non-combustible components in the coal, that are generally stored in open surface ponds or landfills. About 130 million tons of coal ash are produced per year in the United States.

Other Possible Solid Petrochemical Energy Sources

In addition to coal and oil, other related natural carbon sources are known, and some are evidently very abundant in selected locations. These include large tar sand and oil-containing shale deposits in Canada. The pursuit of the possibility of their extraction and use has elicited strong, and sometimes politically charged, emotions.

One of the issues has been the desire to transport the products across the United States to the Gulf Coast, where they would be refined, and then shipped overseas, rather than being made available for consumption domestically.

These are comparatively dilute sources of carbon, and their extraction and conversion into useful fuels is relatively expensive. In addition, they involve the use and consumption of other materials, such as natural gas and water, in the conversion process.

Although very large amounts of this family of solid hydrocarbons are known in a number of places, it must be recognized that they are also depletable resources. The time required for their regeneration in nature is immense, so they can also only be counted upon once.

Crude Oil

Petroleum, or crude oil, is also a fossil fuel, similar to coal; but it has the advantage that it is liquid. This makes it much more versatile for a number of applications. The major use in the United States at the present time is for transportation. It is readily transported using vehicles (ships, trucks, and rail), as well as pipelines, and it can be easily stored in tanks. For a number of years it has been less expensive to extract crude oil, rather than coal, from the earth, although this disparity has varied with both location and time. As readily extracted natural crude oil supplies are consumed, it is generally necessary to dig ever deeper, with greater associated costs.

The specific energy of typical crude oil is about 42 KJkg^{-1} . This is higher than any other fossil fuel. It has become a world commodity, and is shipped all over the world. Refineries convert it to a variety of products, such as heavy fuel oil, diesel fuel, gasoline, kerosene, etc. Subsequently, significant amounts of these liquid materials are also converted into a variety of solid plastics.

Mankind's use of petrochemical fuels based on crude oil as energy sources is actually only quite recent. Table 1 lists a number of the major crude oil discoveries and their dates. These have all occurred in the last century and a half. Thus the "oil age" has been just a recent episode in the history of modern civilization.

Table 1 The discovery of oil—locations and dates

Early discoveries		
	Near Bakku, on the Caspian Sea	About 1849
	Bend, North of Bucharest, Rumania	1857
	Oil Springs, Ontario, Canada	1858
	Drake well near Titusville, PA, USA	1859
First major oil fields discovered		
	Spindletop, near Beaumont, TX, USA	1901
	Others in Oklahoma and California, USA	Shortly thereafter
Discoveries in the Middle East		
	Bahrain	1920
	Kirkuk in Iraq	1927
	Gachsaran in Iran	1935
	Dammam in Saudi Arabia	1938
	Abqaiq in Saudi Arabia	1940
	Ghawar in Saudi Arabia	1948–1949
Alaska, USA		
	Prudhoe Bay	1968
North Sea areas		
	Forties, UK	1970
	Ekofisk, Norway	1971
	Brent, UK	1971
South America		
	Venezuela	1988

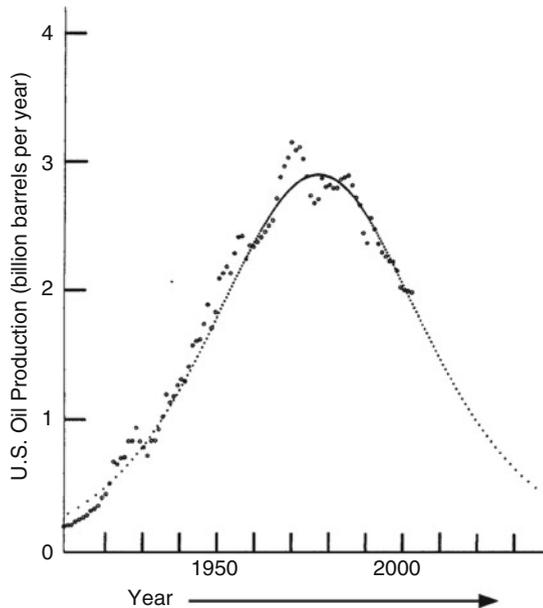
The Problem of the Depletion of Fossil Fuels

As mentioned earlier, fossil fuels are not infinitely available, and the sources that are found become depleted as their contents are removed. It was long thought that this would not become a problem, for new oil fields would be found to replace those that became depleted. Contrary to this, M. King Hubbert published predictions of future oil production in both the United States [1] and the world [2] that indicated that annual oil production would follow bell-shaped curves, reaching a peak, followed by decline in each case.

His predictions were not taken very seriously for some time, all seemed to be going well, with oil production growing every year. But US production peaked in 1970 and decreased as existing fields depleted faster than the rate of discovery.

This is depicted in Fig. 2, which compares actual production to the 1956 prediction by Hubbert that US production would peak about 1970. It is seen that the correspondence is remarkable. Obviously, the United States would be more and more dependent upon imported oil, not just because of its increasing energy demand, but also the decline in its domestic production.

Fig. 2 Relationship between actual annual oil production and the prediction made by Hubbert in 1956. Adapted from [4]



The same question naturally arose concerning the world supply of oil, and many people took the view that there is no problem in this case, as new sources will always be found. Some, however, including M.R. Simmons [3] and K.S. Deffeyes [4]. Believe that the same peak phenomenon is bound to occur, and that the world production peak had already been reached. Hubbert [2] predicted the world production to peak in 2000 and the Deffeyes estimate [4] was 2005. A number of the major known oil fields are now well beyond their production peaks.

The expectation that the world production of readily accessible crude oil would reach a peak in the future, if it had not already done so, provided a great incentive for the development of alternative sources of energy. This is compounded by the fact that the world's population is rapidly expanding. The world's production of oil on a per person basis from the traditional sources, which are primarily in the Middle East, have already reached a peak and is declining.

Thus the long-term crude oil supply situation had been considered until recently to be very bleak. Unlike wood, carbon and petrochemical fossil fuels must be considered to be non-renewable resources; they take millions of years to form. Conservation measures and the search for alternatives to crude oil has become an imperative.

As will be discussed briefly later in this Preface, this situation has changed immensely in the last few years, and these dire predictions have been forgotten.

Natural Gas

Natural gas, which is used for both the generation of electrical power and the production of petrochemicals, consists primarily of methane, CH_4 . It is found associated with liquid fossil fuels and in coal beds. It is also present under the ocean as methane clathrates, as will be mentioned in the next section.

At high pressure underground, natural gas dissolves in oil, and it is often emitted when oil is pumped to the surface, where the pressure is lower. This associated gas is sometimes simply burned at the well sites as "gas flares," for its value is considered to be considerably less than the associated oil. Anyone flying over the Middle East at night can readily identify the oil well areas from the light emitted from these flares. As the price of natural gas has risen, there has been an increasing tendency to capture, rather than simply burning, it.

Oil is typically recovered at depths between 7500 and 15,000 ft below the surface. The deeper the pressure, the higher the temperature, and the larger molecules in the oil become cracked into smaller units. Below about 15,000 ft the oil is cracked down to molecules that have only one carbon atom, i.e., methane, CH_4 .

Thus gas wells are often drilled to depths considerably deeper than those aimed at the extraction of oil.

Early gas wells were actually drilled before the first oil wells. One early successful one was drilled in New York State in 1821. That was 35 years before the famous Drake oil well was established in Northern Pennsylvania.

Drilling gas wells is generally much faster and less expensive than drilling for oil, and there have traditionally been many more gas wells than oil wells in the United States. Information about natural gas production and available reserves is much more difficult to obtain than that for oil. Thus there are no predictions available for natural gas comparable to those using the Hubbert method for the predictions about the oil supply.

In addition to methane, natural gas can contain significant quantities of heavier hydrocarbons, such as ethane, propane, butane, and pentane. Besides these related materials, CO₂, nitrogen, hydrogen sulfide, and helium are also often present. A significant effort is often undertaken to separate some of these more valuable components.

Methane-rich gases can also be produced by the anaerobic decay of non-fossil organic matter, such as manure and the waste in landfills. These are typically called *bio-gas*.

Methane released into the atmosphere is a potent greenhouse gas and is generally considered to be a pollutant. It gradually becomes oxidized to form CO₂ and water, which are also greenhouse gases. The kinetics of this process are such that methane that enters the atmosphere can be considered to have a half-life of about 7 years.

Natural gas can be used as a fuel for electricity generation in steam turbines and higher temperature gas turbines. It burns cleaner than either petroleum or coal and produces less CO₂ per unit energy obtained. For an equivalent amount of heat, natural gas produces 30 % less CO₂ than burning petroleum, and 45 % less than burning coal. It is therefore generally considered to be the cleanest of the fossil fuels. It can be used for heating and cooking in homes, and also as a vehicle fuel instead of gasoline or diesel fuel. Natural gas consumption surpassed that of crude oil in the United States in 1984.

The standard unit of volume of natural gas is 1000 cubic feet (28.3 m³) at room temperature and pressure. This gives about one million BTUs, which is approximately 1 GJ of energy. The energy content of 6000 cubic feet (169.8 m³) of gas is equivalent to one barrel of crude oil.

Some hydrogen produced from natural gas is also reacted with nitrogen in the high pressure Haber process to produce ammonia, an important feedstock for the production of fertilizers. Some 3–5 % of the world natural gas production is used for this purpose.

Natural gas can be readily transported in pipelines. It also can be liquefied, and stored and transported in refrigerated tanks, even across oceans in ships. Russia is currently the largest producer of natural gas in the world, and a large source of oil. Some of this gas, as well as oil, is exported to Western Europe through several large pipelines. In 2007 the European Union imported 100.7 million tons of oil-equivalent natural gas, 38.7 % of its total gas import, and 185 million tons of

crude oil, 32.6 % of its total oil imports, from Russia. Two countries, Germany and Italy, accounted for about half of these totals.

About 80 % of these travel through pipelines that cross Ukrainian soil. This leads to the potential for serious problems for countries further to the West. There have been significant disputes between Russia and the Ukraine in recent years that have led to the cut-off of supplies to both the Ukraine and countries in Western Europe.

As in the case of oil, the supply of natural gas in the United States has changed greatly in the last few years, due to the development of fracking technology. This will be briefly discussed later in this Preface.

Hydrogen

Hydrogen is not actually an energy source, as it is obtained by using energy. Instead, it is generally described as being an energy carrier. Some 9–10 million tons of hydrogen are now produced in the United States per year. It is used for many purposes, as a feedstock and intermediate in chemical production, petroleum refining, and metals treating. Its use to convert heavy petroleum into lighter fractions is called *hydrocracking*. The current applications in transportation and as the fuel in fuel cells represent a very minor fraction of the total.

There are several methods by which hydrogen is currently obtained. The least expensive of these, which accounts for some 95 % of the total, is the production of hydrogen by the treatment of natural gas at elevated temperatures. The composition of the natural gas obtained from the earth varies from place to place. It can contain significant amounts of sulfur in some locations. In some cases it is obtained as a by-product of the extraction of petroleum. In the Middle East the natural gas that is extracted along with the petroleum is often thrown away, for its value may not be sufficient to justify the cost of containing and transporting it. As a result, it is burned, or “flared.” The lights from this process can be clearly seen when flying over this part of the world at night.

Hydrogen can also be obtained in other ways. One of the most prominent is by the electrolysis of water, which currently accounts for about 4 % of the total. These alternatives will be discussed in Chap. 8.

Methane Clathrates

Another potentially immense source of energy that might be used in the future is related to the presence of large amounts of *methane clathrate* deep in the oceans. This material is also sometimes known as *methane hydrate* or as *methane ice*. It can be described as a crystalline solid H₂O-ice structure within which methane is trapped.

The widespread existence of such materials was first recognized during the 1960s and 1970s, and they are now recognized to be common constituents of the shallow (<2000 m) marine geosphere, where they occur both as deep sedimentary deposits and as outcrops on the ocean floor. They are typically found in the ocean at depths greater than 300 m, and where the bottom water temperature is around 2 °C. They have been found to be widespread along the continental shelves and are also apparently present in deep lakes, such as Lake Baikal in Siberia.

In addition, methane clathrates have been found trapped in continental rocks of sandstone and siltstone at depths of less than 800 m in cold areas, such as Alaska, Siberia, and Northern Canada.

They are generated as the result of bacterial degradation of organic matter in low oxygen aqueous environments. It is believed that large volumes of methane may occur as bubbles of free gas below the zone of clathrates. They are stable up to about 0 °C, above which they decompose to form liquid water and gaseous methane, CH₄. At higher pressures they can remain stable to higher temperatures.

A typical deposit composition has 1 mol of methane for 5.75 mol of water. As a result, the melting of 1 L of solid clathrate produces 168 L of methane gas at 1 atm pressure.

There are two general methods that have been employed to extract the methane from these clathrates. One is by heating, and the other is by reducing the pressure. The latter evidently requires significantly less energy.

Estimates of the amount of clathrate hydrates on the earth have varied widely and have decreased somewhat with time. Recent values run from 1 to 5×10^{15} cubic meters. These values are equivalent to 500–2500 gigatons of carbon, values smaller than the estimate of 5000 gigatons of carbon for all other fossil fuel reserves, but substantially greater than current estimates of natural gas (also mostly methane) reserves.

Although methane clathrates are potentially a very important source of fuel, there has evidently been only one commercial development to date, near Norilsk in Russia. Research and development projects are current underway in both Japan and China.

Since these deposits are very large in some cases, they certainly represent potentially important energy resources. The incentives to develop economical methods to recover the trapped fuel within them are immense.

Chemically Derived Fuels

In addition to the depletable energy sources found in nature, a significant amount of attention is now being given to the production of liquid fuels from renewable sources besides wood.

It has been known for hundreds of years in Asia and Europe that an oil can be produced that can be used to burn in lamps, as a machine lubricant, and also for cooking, by simply pressing rapeseed. More recently, it was found that a modification

of this natural oil can be used as a diesel fuel. This plant, called “Raps” in German, has beautiful bright yellow blossoms in the spring. They provide a striking vista in large areas of the landscape in Northern Germany, where the author lived for a number of years. This material is called “Canola” in the United States and Canada.

There are a number of other biological materials that can provide useful fuels. There are two general types of such *agrofuels*. One is to use oilseed crops, such as rapeseed, soy beans, palm oil, and some seeds and nuts that contain high amounts of vegetable oil. *Jatropha* nuts are up to 40 % oil.

The other type includes crops that are high in sugar (e.g., sugar cane, sugar beet, and sweet sorghum) or starch (e.g., corn or switch grass (*panicum virgatum*)). These go through a yeast fermentation process to produce ethyl alcohol that can be used as a liquid fuel. Such biofuels currently provide 45 % of Brazil’s fuel, where all autos run on ethanol.

When the prices of petrochemical fuels are high, the possibility of producing an economically competitive alternative fuel using corn becomes attractive. This has resulted in the diversion of a substantial fraction of the food corn production in that direction. In turn, the costs of related foods to the consumer have escalated, and become a political problem.

A further fuel source that is beginning to become economically attractive on a modest scale involves the use of animal fats. Whale oil, obtained from the fat (blubber) of whales, was the first animal oil to become commercially viable for use as a fuel, being used as a lamp oil, and a candle wax. Transesterification (catalytically reacting fats with short-chain aliphatic alcohols) can be used to produce useful liquid fuels from a number of different types of animal waste. One of the attractive features of this process is that it represents a convenient method for disposing of otherwise unusable animal waste from such places as meat processors and high volume chicken restaurants.

But ramping up the availability of these alternatives to the point that they make major contributions to the overall energy supply picture takes an appreciable period of time.

Recently Discovered Large Natural Gas and Oil Sources

Although the subject of this book is energy storage, not energy sources, a very important recent development in the latter area deserves mention here. It will surely have a very significant influence upon the energy supply, distribution, and storage in the United States.

Advances in drilling techniques recently resulted in the recognition that it is possible to obtain large amounts of natural gas and/or oil from underground shale layers. The existence of shale layers, which typically lie more than a mile below the surface, and that are known to contain gas, and also oil in some locations, has been known for some time. But it was long considered to be too difficult and expensive to extract significant quantities of useful fuels from them using normal drilling methods.

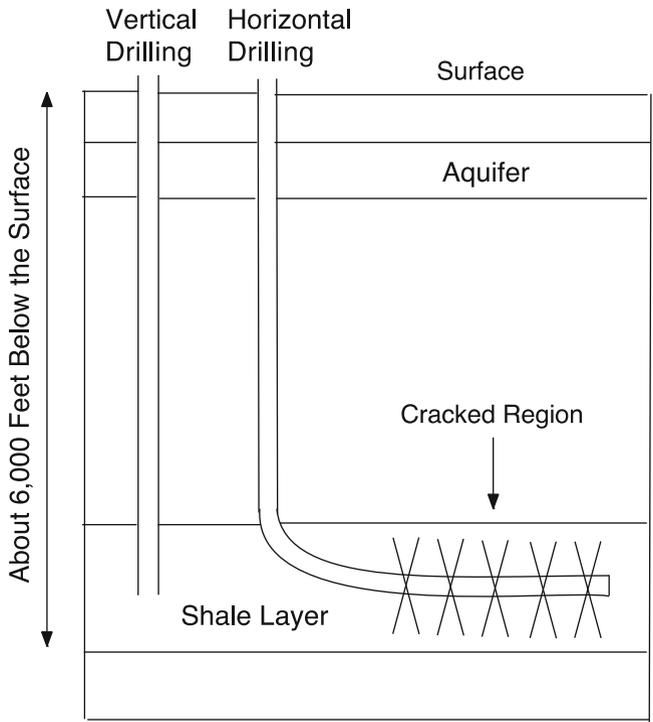


Fig. 3 Schematic representation of the difference between normal vertical drilling and horizontal drilling

The change in this picture resulted from the development of a new drilling and extraction strategy, called “fracking,” which involves drilling horizontally into a shale layer, rather than through it [5,6]. This is illustrated schematically in Fig. 3.

A mixture of water and sand is forced into the shale formation at very high pressure. This causes many small fractures, or cracks, in the shale. These fractures would normally be expected to close as soon as the water pressure is decreased, but the presence of the fine sand, which goes into the cracks, causes them to remain open. As a result, significant quantities of the trapped gas and/or oil become accessible.

Regular oil and gas production using this method started in 2005. The oil and gas industry is now making very large investments to get access to this potentially large domestic source of natural gas and oil, and the rate of production is increasing rapidly.

This involves the injection of large quantities of water into the shale—up to 4–6 million gallons of fresh water per well. Various estimates indicate 15–35 % of the water and chemicals that are injected return to the surface as “flowback.” This water has picked up some chemicals, generally sodium, magnesium, and calcium chlorides, which results in a significant increase in its salinity. Ground water tends to get

saltier at greater depths. As a result, this water is not suitable for surface discharge or agricultural use. The least costly method for its disposal is permanent injection into a nearby deep well, but such wells must be carefully cased and cemented. There have been numerous examples of small earthquakes related to this water injection.

There are also some additional tricks that make this process much more efficient. They are typically proprietary, but often include materials such as a cross-linking “thickening agent,” typically a sugar, to increase the viscosity, a biocide such as glutaraldehyde, a polyacrylamide “friction reducer,” a phosphonate detergent scale inhibitor, and a surfactant.

Well construction can be quite fast, with an average time to production being less than a month. A method called “pad drilling,” in which a number—15 or more—of wells are drilled in different directions from a single pad, has become common.

Production from shale gas wells typically falls off rapidly with time—often dropping 60–80 % in the first year, followed by a slower asymptotic decline. Conventional oil wells typically decline more slowly, some 25–40 % in the first year. Further drilling and re-fracking at greater horizontal distances is often done as production declines, for this is much less expensive than drilling new wells.

As was discussed earlier, the combustion of natural gas produces only about half as much carbon dioxide as the combustion of oil. Thus it is often considered to be a “bridge” or “transition” fossil fuel during the transition from the dependence upon imported oil to increased use of more environmentally friendly local energy sources.

The recent development of these large new oil and gas sources in the United States has also caused the construction of a number of previously planned new coal-fired power plants to be postponed or cancelled, for they cannot compete economically. Gas plants cost less to build and are cheaper to operate. In addition, it is much easier to get permits for new construction.

The introduction of this technology has caused economic windfalls and sudden labor shortages in some previously quiet locations. The extreme current example of this is in North Dakota, but similar economic rejuvenation is occurring in other areas, including some in the Midwest, where the metals-based manufacturing industry has been in serious decline for a number of years. North Dakota is now the second-biggest oil producing state, after Texas, in the United States.

There is not enough pipeline capacity to handle the rate of oil production, so a large amount of the oil is carried by the local railroads, which have had a number of serious spills and fires. This competition for the available transportation mechanisms has also resulted in difficulties getting the normal local farming products to market.

The development of fracking technology has resulted in a major change in the international energy picture. Instead of being dependent upon imported oil from the Middle East, the United States is now beginning to become a major oil exporter. This is expected to continue for a long time. Recent data on the production of gas and oil in the United States are shown in Fig. 4.

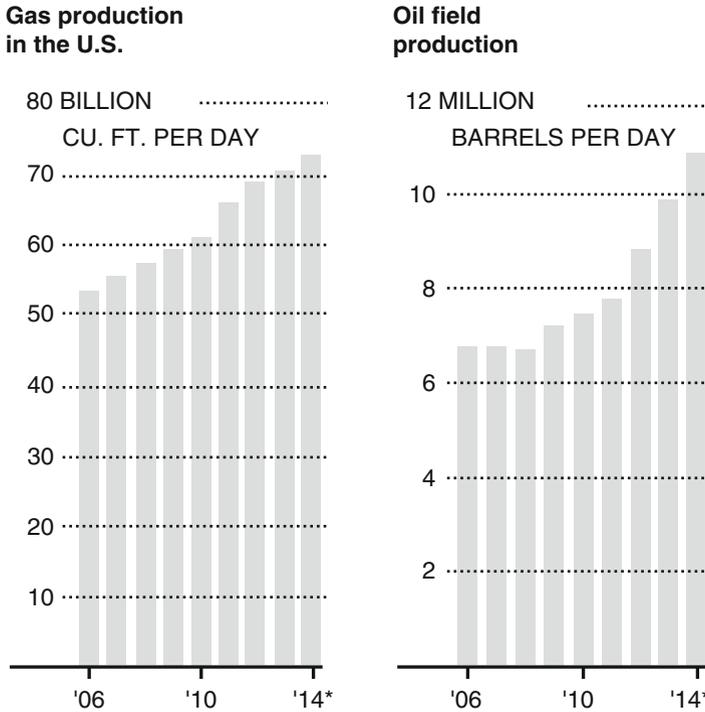


Fig. 4 Recent growth of gas and oil production in the United States

Other Alternative Energy Sources

A number of other energy sources are being pursued, and several of these are gradually taking over some of the energy demand burden. Among the prominent alternatives are solar and wind energy technologies. Others involve the use of geothermal sources, collected rainfall, and making use of both tidal variations and currents in the world’s oceans. A further approach to the extraction of energy from natural phenomena involves various schemes to harness the power of ocean waves [7].

There is continued interest in the use of nuclear fission to produce heat, and its use to supply electricity. In this latter case, in addition to cost, there is the persistent, and extremely serious, problem of what to do with the inevitable long-lived radioactive waste. Until the waste problem is solved, this approach will continue to be extremely dangerous.

There is also great concern about the safety of large nuclear energy facilities. There was an accident at the Three Mile Island plant in the United States in March 1979 that involved a partial nuclear meltdown of one of the two nuclear reactors at that site. But, fortunately, this did not result in a major disaster, as it was relatively

well contained, although there was the release of a significant amount of radiation. The cleanup cost was estimated to have been about one billion dollars.

A much larger disaster occurred at Chernobyl in the Ukraine, which was then part of the Soviet Union, in April 1986. A fire and an explosion caused large quantities of radioactive particles to go high into the atmosphere. This radioactive cloud moved to the North, across Scandinavia, and then down into Northern Europe. Radioactivity from this nuclear disaster was first detected in Sweden, 2 days before it was publicly reported in the USSR.

High levels of radioactivity soon were found in large areas of Western Europe, especially in Sweden and Norway, as well as in the USSR. The Sami (also known as Lapps, or Laplanders), who live in Northern Sweden and Norway, and whose livelihood has traditionally been based upon reindeer—herding, were especially affected by the radiation. In addition to the health risks to people, lichen, the food eaten by the reindeer, became seriously contaminated, decimating their herds. There was also widespread contamination of other food sources. Radioactive fallout got into freshwater lakes and inland forests, contaminating sheep, cows (and their milk), fish, wild game, and berries, especially in Sweden. As a result, many people were moved large distances, and forced to take up other activities.

The most dangerous pollutant was cesium 137, which has a half-life of 30 years, and it is expected that the radioactivity in the most contaminated areas will not drop to “safe” levels for at least 20 years. Eventual full disposal of the radioactivity will take up to 50 years.

In an attempt to prevent further escape of radioactive materials from the Chernobyl atomic power site some 5 million kg of lead and stone were dropped onto the reactor as rapidly as possible. A massive steel and concrete structure, called a sarcophagus, which was constructed to cover the reactor and to limit radioactive contamination of the environment material is gradually decaying, and in danger of collapsing. In 1996 it was decided to replace it by a much larger two-part containment structure by 2006. This is currently still under construction nearby, where the radiation level is significantly lower than in the reactor area. The two parts will be moved over the top of the original structure when they are completed; this is now scheduled to happen in 2015. This new containment structure, one of the largest engineering projects ever undertaken, will be 360 ft tall and 843 ft wide, and it is estimated that it will cost some 1.5 billion Euros, or about 2 billion US dollars.

After the Chernobyl explosion a large “exclusion zone,” which could no longer be inhabited, was defined. It had an initial radius of about 20 miles around the nuclear power plant. This non-habitable area has subsequently been expanded and now covers about 1000 mile². Over 120,000 people were permanently evacuated from Chernobyl and nearby Pripjat, as well as many smaller communities in that area.

Another major nuclear disaster happened in the Fukushima Daiichi coastal area of Japan in March 2011, where a large tsunami wave, caused by a nearby magnitude 9 earthquake, overwhelmed the plant’s seawall, and resulted in the meltdown of three of the power plant’s six nuclear reactors. Fortunately, the other three were not in service at that time.

During the first day after this incident 134,000 people were evacuated from the nearby area, and this number was later increased by an additional 354,000 from a 12 mile radius exclusion zone.

Relatively little radioactive material went into the atmosphere in this case, compared to what happened in the Chernobyl disaster. However, the power plant was flooded by the tsunami wave, and a large amount of water swept into the site. This water became radioactive and is seriously hindering the cleanup process. More water is continuing to flow through the site and into the nearby ocean, and there is much concern about radioactivity in both the water and the fish in it. The ocean currents in this area are relatively strong, and it is expected that slightly radioactive water will be found as far away as the Western United States.

In order to stop the continued flow of this radioactive material into the ocean, there have been plans to construct a 2400 ft long steel and concrete wall between the site and the ocean, reaching 100 ft below ground. An alternative, the establishment of an underground ice wall, has also been discussed. Cleanup is expected to take decades. And as in the Chernobyl case, the major concern has been contamination by radioactive caesium 137, because of its long half-life.

These disasters have caused a number of nations to become wary of nuclear energy. As a result of the serious meltdown of the reactors in the Fukushima nuclear plant, the Japanese government decided to shut down its remaining nuclear power generators, which had been providing about 30 % of its total electrical power. This has resulted in increased dependence upon coal and natural gas energy sources, and a corresponding increase in the emission of greenhouse gases. Other technologies are also being promoted, including large groups of offshore wind turbines, and increased use of solar panels.

Germany decided to shut down eight of its nuclear reactors and to close the remaining nine by 2022. It is planned to have 30 % of its electric grid converted to solar (mostly in the South) and Wind (mostly in the North) sources in about 15 years. Residents receive a guaranteed high price for the energy that they generate, and over 1.4 million German homes currently generate electricity from either solar or wind sources. The local prices of solar and wind energies have already dropped 80 and 55 % from what they were in the year 2000.

Italy held a national referendum in which 94 % voted against the government's plan to build new nuclear power plants. The same happened in Switzerland, and later, in Belgium.

In France, the strongly pro-nuclear government was defeated in a national election, with 70 % of the public opposing nuclear energy in some polls. It was replaced by a government that promised to radically reduce France's reliance on nuclear power.

Plans for the introduction of nuclear power were abandoned in Malaysia, the Philippines, Kuwait, and Bahrain, or radically changed, as in Taiwan. China suspended its nuclear development program, but restarted it on a reduced basis in late 2012, with the government approving a "small number" of projects in each of the following 5 years. The initial plan had been to increase the nuclear contribution from 2 to 4 % of electricity by 2020, but renewable energy already supplied 17 % of

China's electricity and, post-Fukushima, it seemed likely that most of the 15 % of non-fossil energy that China aims to use by 2020 will be from renewables.

On the other hand, new nuclear energy projects are proceeding in some countries. The United Kingdom is planning a significant expansion, as are Russia, India, and South Korea.

A significant aspect of most of these alternative energy sources is that they tend to be time-dependent. The availability of water for hydroelectric and other uses varies with the time of the year, as well as the weather. The sun rises and sets, winds come and go, and tidal flows are periodic. This leads to the problem of either matching the time dependence of the energy source with the time dependence of energy needs, or the development and use of effective energy storage methods.

On the macroscopic scale, one of the ways that this is currently accomplished is to use the large-scale electrical transmission grid as a buffer. This grid is generally supplied by the use of fossil fuels such as coal or crude oil, although nuclear or hydroelectric sources are also employed in some locations. Energy from intermittent sources can be fed into this large system when its capacity is available, reducing the requirements from the normal grid-supplying sources. This can be especially useful if energy from such alternative sources is available at times when the grid's customers' requirements are high, and the cost of additional generating capacity is quite high.

The need for energy from the electrical grid generally depends upon the time of day and the day of the week. It also can vary greatly with the weather and time of year. The large-scale energy storage problem of matching supply with need, sometimes called "load leveling" and "peak shaving," will be dealt with later in this text. There are many other non-steady-state uses.

An entirely different problem arises when the energy is required for vehicles, or smaller, and likely portable uses, such as computers and telephones. In such cases, energy transfer occurs in one direction, and the storage device is likely charged, either directly, or indirectly, from the electrical grid.

Thus it can be seen that there are many different types of needs for energy storage, requiring a variety of solutions. These topics will be addressed in this book.

The very serious problem of the depletion of the traditional energy sources and the need to find and develop alternatives has attracted the attention of, and led to action by, governmental bodies worldwide. An important example in the United States was the Energy Independence and Security Act (EISA) that was passed by the Congress and became law in December 2007 [8]. The intent of this law was to increase energy efficiency and the availability of renewable energy. It included provisions to improve the efficiency of vehicles, appliances, and lighting, and to increase the production of biofuels. It also called for accelerated research and development on other energy sources and on related energy storage methods.

Further action in these directions was mandated in the American Recovery and Reinvestment Act of 2009 [9]. In addition to large increases in funding for work on energy efficiency and renewable energy, as well as research and development in energy-related areas, a considerable amount of money was allocated for the

development of manufacturing facilities in the United States related to electrochemical energy storage.

It is clear that energy storage will be an increasingly important component of the overall energy supply and use picture in the future. This will be particularly critical as the alternative technologies, such as solar and wind sources, where energy production is intermittent, become more widespread.

It is the goal of this book to provide an understanding, rather than a mere description, of the various mechanisms by which energy can be stored for later or alternate use.

Stanford, CA, USA

Robert A. Huggins

Acknowledgements

The author gladly acknowledges with gratitude the important contributions made to the development of the understanding in this area by his many students and associates in the Solid State Ionics Laboratory of the Department of Materials Science at Stanford University over many years, as well as those in the Center for Solar Energy and Hydrogen Research (ZSW) in Ulm, Germany, and in the Faculty of Engineering of the Christian Albrechts University in Kiel, Germany.

References

1. Hubbert MK (1956) Nuclear Energy and the Fossil Fuels. American Petroleum Institute Drilling and Production Practice Proceedings. p 5
2. Hubbert MK (1969) Energy Resources. In: Freeman WH (ed) Resources and Man. National Research Council, Committee on Resources and Man. p 196
3. Simmons MR (2005) Twilight in the Desert. John Wiley
4. Deffeyes KS (2005) Beyond Oil. Hill and Wang
5. Rao V (2012) Shale Gas. RTI Press
6. Zuckerman G (2013) The frackers. Penguin
7. Cruz J (ed) (2008) Ocean Wave Energy: Current Status and Future Perspectives. Springer
8. Energy Independence and Security Act of 2007, which became law in the United States in December, 200.
9. American Recovery and Reinvestment Act of 2009, which became law in the United States in February, 200.

Contents

1	Introduction	1
1.1	Introduction	1
1.2	Storage in the Fuel Distribution System	2
1.3	Periodic Storage	3
1.3.1	Long-Term, or Seasonal, Storage	3
1.3.2	Daily and Weekly Storage	3
1.4	The Problem of Load Leveling	4
1.5	Methods That Can Be Used to Reduce the Magnitude of the Variations in Energy Demand	5
1.6	Short-Term Transients	7
1.7	Portable Applications That Require Energy Storage	8
1.7.1	Storage Methods for Use with Portable Electronic Devices	8
1.7.2	Energy Use and Storage in Vehicles	8
1.8	Hydrogen Propulsion of Vehicles	9
1.9	Temperature Regulation in Buildings	10
1.10	Improved Lighting Technologies	11
1.11	The Structure of This Book	12
	References	12
2	General Concepts	13
2.1	Introduction	13
2.2	The Mechanical Equivalent of Heat	13
2.3	The First Law of Thermodynamics—Conservation of Energy	14
2.4	Enthalpy	14
2.5	Entropy	15
2.5.1	Thermal Entropy	15
2.5.2	Configurational Entropy	16
2.6	The Energy Available to Do Work	16
2.7	The Temperature Dependence of G , H , and S	17

2.8	Irreversible and Reversible Storage Modes	18
2.9	The Carnot Limitation	18
2.10	Energy Quality	18
	References	19
3	Thermal Energy Storage	21
3.1	Introduction	21
3.2	Sensible Heat	22
3.3	Latent Heat	23
	3.3.1 Inorganic Phase Change Materials	24
	3.3.2 Organic Phase Change Materials	26
3.4	Quasi-Latent Heat	27
3.5	Heat Pumps	27
	References	27
4	Reversible Chemical Reactions	29
4.1	Introduction	29
4.2	Types of Non-congruent Chemical Reactions	30
	4.2.1 Insertion Reactions	30
	4.2.2 Formation Reactions	31
	4.2.3 Decomposition Reactions	32
	4.2.4 Displacement Reactions	32
4.3	Phase Diagrams	33
	4.3.1 The Gibbs Phase Rule	33
	4.3.2 Binary Phase Diagrams	34
	4.3.3 The Lever Rule	37
	4.3.4 Three-Phase Reactions in Binary Systems	38
	4.3.5 Examples of Materials Systems with Peritectic Reactions	39
	4.3.6 Binary Systems That Contain Eutectic Reactions	41
4.4	Thermal Effects Related to Liquid and Solid Reactions	43
4.5	Thermal Effects Related to Reversible Gas Phase Reactions	45
	References	48
5	Energy Storage in Organic Fuels	49
5.1	Introduction	49
5.2	Storage of Energy in Living Biomass	49
5.3	Storage via Animals	51
5.4	Hard Biomass	52
5.5	Synthetic Liquid Fuels	52
5.6	Gaseous Fuels Stored as Liquids	53
5.7	The Energy Content of Various Materials Used as Fuels	53
	References	54

6	Mechanical Energy Storage	55
6.1	Introduction	55
6.2	Potential Energy Storage	55
6.3	Energy Storage in Pressurized Gas	57
6.4	Potential Energy Storage Using Gravity	59
6.5	Hydroelectric Power	60
6.6	Pumped-Hydro Storage	61
6.7	Use of the Kinetic Energy in Moving Water	63
6.8	Kinetic Energy in Mechanical Systems	63
	6.8.1 Linear Kinetic Energy	63
	6.8.2 Rotational Kinetic Energy	64
6.9	Internal Structural Energy Storage	68
	Reference	68
7	Electromagnetic Energy Storage	69
7.1	Introduction	69
7.2	Energy Storage in Capacitors	70
	7.2.1 Energy in a Parallel Plate Capacitor	70
7.3	Electrochemical Charge Storage Mechanisms	72
	7.3.1 Electrostatic Energy Storage in the Electrical Double-Layer in the Vicinity of an Electrolyte/Electrode Interface	72
	7.3.2 Underpotential Faradaic Two-Dimensional Adsorption on the Surface of a Solid Electrode	73
	7.3.3 Faradaic Deposition that Results in the Three-Dimensional Absorption of the Electroactive Species into the Bulk Solid Electrode Material by an Insertion Reaction	74
	7.3.4 Faradaically-Driven Reconstitution Reactions	76
7.4	Comparative Magnitudes of Energy Storage	77
7.5	Importance of the Quality of the Stored Energy	78
7.6	Transient Behavior of a Capacitor	79
7.7	Modeling Transient Behavior of Electrochemical Systems Containing Capacitive Components Using Laplace Transforms	81
	7.7.1 Introduction	81
	7.7.2 Use of Laplace Transform Techniques	82
	7.7.3 Simple Examples	82
7.8	Energy Storage in Magnetic Systems	85
	7.8.1 Energy in a Material in a Magnetic Field	85
	7.8.2 Energy Storage in Superconducting Magnetic Systems	90
	7.8.3 Superconductive Materials	91
	References	93

8	Hydrogen Storage	95
8.1	Introduction	95
8.2	The Production of Hydrogen	96
8.2.1	The Steam Reforming Process	96
8.2.2	The Reaction of Steam with Carbon	98
8.2.3	Electrolytic Production of Hydrogen	100
8.2.4	Thermal Decomposition of Water to Produce Hydrogen	103
8.2.5	Chemical Extraction of Hydrogen from Water	104
8.2.6	Additional Approaches to the Production of Hydrogen	107
8.3	Governmental Promotion of the Use of Hydrogen	108
8.4	Current On-Board Hydrogen Storage Alternatives	110
8.4.1	Storage of Gaseous Hydrogen in High-Pressure Tanks	110
8.4.2	Storage of Liquid Hydrogen in Insulated Tanks	110
8.4.3	Storage of Hydrogen as Protons in Solids: Metal Hydrides	111
8.5	Other Approaches to Hydrogen Storage	112
8.5.1	Hydrogen from the Decomposition of Materials Containing Hydride Anions	112
8.5.2	Ammonia and Related Materials as Hydrogen Storage Media	113
8.5.3	Storage of Hydrogen in Reversible Organic Liquids	115
8.6	The Question of Safety	117
	References	117
9	Introduction to Electrochemical Energy Storage	119
9.1	Introduction	119
9.2	Simple Chemical and Electrochemical Reactions	120
9.3	Major Types of Reaction Mechanisms in Electrochemical Cells	125
9.3.1	Formation Reactions	125
9.3.2	Displacement Reactions	127
9.3.3	Insertion Reactions	128
9.4	Important Practical Parameters	129
9.4.1	The Operating Voltage and the Concept of Energy Quality	130
9.4.2	The Charge Capacity	132
9.4.3	The Maximum Theoretical Specific Energy (MTSE)	133

9.4.4	Variation of the Voltage as Batteries Are Discharged and Recharged	133
9.4.5	Cycling Behavior	135
9.4.6	Self-Discharge	136
9.5	General Equivalent Circuit of an Electrochemical Cell	136
9.5.1	Influence of Impedances to the Transport of Ionic and Atomic Species Within the Cell	138
9.5.2	Influence of Electronic Leakage Through the Electrolyte	138
9.5.3	Transference Numbers of Individual Species in an Electrochemical Cell	140
9.5.4	Relation Between the Output Voltage and the Values of the Ionic and Electronic Transference Numbers	141
9.5.5	Joule Heating Due to Self-Discharge in Electrochemical Cells	141
9.5.6	What If Current Is Drawn from the Cell?	142
	References	144
10	Principles Determining the Voltages and Capacities of Electrochemical Cells	145
10.1	Introduction	145
10.2	Thermodynamic Properties of Individual Species	145
10.3	A Simple Example: The Lithium/Iodine Cell	147
10.3.1	Calculation of the Maximum Theoretical Specific Energy	149
10.3.2	The Temperature Dependence of the Cell Voltage	150
10.4	The Shape of Discharge Curves and the Gibbs Phase Rule	151
10.5	The Coulometric Titration Technique	157
	References	160
11	Binary Electrodes Under Equilibrium or Near-Equilibrium Conditions	161
11.1	Introduction	161
11.2	Relationship Between Phase Diagrams and Electrical Potentials in Binary Systems	162
11.3	A Real Example, the Lithium–Antimony System	163
11.4	Stability Ranges of Phases	168
11.5	Another Example, the Lithium–Bismuth System	169
11.6	Coulometric Titration Measurements on Other Binary Systems	171
11.7	Temperature Dependence of the Potential	171
11.8	Application to Oxides and Similar Materials	173

11.9	Ellingham Diagrams and Difference Diagrams	173
11.10	Comments on Mechanisms and Terminology	177
11.11	Summary	178
	References	179
12	Ternary Electrodes Under Equilibrium or Near-Equilibrium	
	Conditions	181
12.1	Introduction	181
12.2	Ternary Phase Diagrams and Phase Stability Diagrams	181
12.3	Comments on the Influence of Sub-triangle Configurations in Ternary Systems	183
12.4	An Example: The Sodium/Nickel Chloride “Zebra” System	186
12.5	A Second Example: The Lithium-Copper-Chlorine Ternary System	189
	12.5.1 Calculation of the Voltages in this System	190
	12.5.2 Experimental Arrangement for Lithium/Copper Chloride Cells	193
12.6	Calculation of the Maximum Theoretical Specific Energies of Li/CuCl and Li/CuCl ₂ Cells	194
12.7	Specific Capacity and Capacity Density in Ternary Systems	195
12.8	Another Group of Examples: Metal Hydride Systems Containing Magnesium	195
12.9	Further Ternary Examples: Lithium-Transition Metal Oxides	202
12.10	Ternary Systems Composed of Two Binary Metal Alloys	206
	12.10.1 An Example, the Li-Cd-Sn System at Ambient Temperature	206
12.11	What About the Presence of Additional Components?	207
12.12	Summary	207
	References	208
13	Potentials	209
13.1	Introduction	209
13.2	Terminology	210
13.3	Potential Scales	211
13.4	Electrical, Chemical, and Electrochemical Potentials in Metals	211
13.5	Relation to the Band Model of Electrons in Solids	218
13.6	Potentials in Semiconductors	218
13.7	Interactions Between Different Materials	219
13.8	Junctions Between Two Metals	220
13.9	Junctions Between Metals and Semiconductors	221

13.10	Selective Equilibrium	222
13.11	Reference Electrodes	223
13.12	Reference Electrodes in Nonaqueous Lithium Systems	223
13.12.1	Use of Elemental Lithium	223
13.12.2	Use of Two-Phase Lithium Alloys	224
13.13	Reference Electrodes in Elevated Temperature Oxide-Based Systems	224
13.13.1	Gas Electrodes	225
13.13.2	Polyphase Solid Reference Electrodes	225
13.14	Relations Between Binary Potential Scales	226
13.15	Potentials in the Ternary Lithium: Hydrogen: Oxygen System	227
13.16	Lithium Cells in Aqueous Electrolytes	228
13.17	Significance of Electrically Neutral Species	228
13.18	Reference Electrodes in Aqueous Electrochemical Systems	229
13.19	Historical Classification of Different Types of Electrodes in Aqueous Systems	231
13.19.1	Electrodes of the First Kind	231
13.19.2	Electrodes of the Second Kind	232
13.20	The Gibbs Phase Rule	234
13.21	Application of the Gibbs Phase Rule to Reference Electrodes	235
13.21.1	Nonaqueous Systems	235
13.21.2	Aqueous Systems	235
13.22	Systems Used to Measure the pH of Aqueous Electrolytes	237
13.23	Electrodes with Mixed-Conducting Matrices	238
13.24	Closing Comments on Reference Electrodes	239
13.25	Potentials of Chemical Reactions	240
13.25.1	Introduction	240
13.25.2	Relation Between Chemical Redox Equilibria and the Potential and Composition of Insertion Reaction Materials	241
13.25.3	Other Examples	242
13.25.4	Summary	244
13.26	Potential and Composition Distributions Within Components of Electrochemical Cells	244
13.26.1	Introduction	244
13.26.2	Relevant Energy Quantities	244
13.26.3	What Is Different About the Interior of Solids?	245
13.26.4	Relations Between Inside and Outside Quantities	246
13.26.5	Basic Flux Relations Inside Phases	246
13.26.6	Two Simple Limiting Cases	247
13.26.7	Three Configurations	247
13.26.8	Variation of the Composition with Potential	247

13.26.9	Calculation of the Concentrations of the Relevant Defects in a Binary Solid MX That Is Predominantly an Ionic Conductor	248
13.27	Defect Equilibrium Diagrams	250
13.27.1	Approximations Relevant in Specific Ranges of Composition or Activity	250
13.27.2	Situation in Which an Electrical Potential Difference Is Applied Across a Solid Electrolyte Using Electrodes That Block the Entry and Exit of Ionic Species	253
13.27.3	The Use of External Sensors to Evaluate Internal Quantities in Solids	255
13.27.4	Another Case, A Mixed Conductor in Which the Transport of Electronic Species Is Blocked	255
13.27.5	Further Comments on Composite Electrochemical Cells Containing a Mixed Conductor in Series with a Solid Electrolyte	257
13.28	Transference Numbers of Particular Species	259
	References	260
14	Insertion Reaction Electrodes	261
14.1	Introduction	261
14.2	Examples of the Insertion of Guest Species into Layer Structures	263
14.3	Floating and Pillared Layer Structures	264
14.4	More on Terminology Related to the Insertion of Species into Solids	264
14.5	Types of Inserted Guest Species Configurations	265
14.6	Sequential Insertion Reactions	266
14.7	Co-insertion of Solvent Species	269
14.8	Insertion into Materials with Parallel Linear Tunnels	270
14.9	Changes in the Host Structure Induced by Guest Insertion or Extraction	272
14.9.1	Conversion of the Host Structure from Crystalline to Amorphous	272
14.9.2	Dependence of the Product upon the Potential	274
14.9.3	Changes upon the Initial Extraction of the Mobile Species	274
14.10	The Variation of the Potential with Composition in Insertion Reaction Electrodes	275
14.10.1	Introduction	275
14.10.2	The Variation of the Electrical Potential with Composition in Simple Metallic Solid Solutions	276
14.10.3	Configurational Entropy of the Guest Ions	277

14.10.4	The Concentration Dependence of the Chemical Potential of the Electrons in a Metallic Solid Solution	278
14.10.5	Sum of the Effect of These Two Components upon the Electrical Potential of a Metallic Solid Solution	278
14.10.6	The Composition Dependence of the Potential in the Case of Insertion Reactions That Involve a Two-Phase Reconstitution Reaction	280
14.11	Final Comments	282
	References	283
15	Electrode Reactions That Deviate from Complete Equilibrium . . .	285
15.1	Introduction	285
15.2	Stable and Metastable Equilibrium	285
15.3	Selective Equilibrium	287
15.4	Formation of Amorphous vs. Crystalline Structures	288
15.5	Deviations from Equilibrium for Kinetic Reasons	290
16	Primary, Non-rechargeable Batteries	291
16.1	Introduction	291
16.2	The Common Zn/MnO ₂ “Alkaline” Cell	291
16.2.1	Introduction	291
16.2.2	Thermodynamic Relationships in the H-Zn-O System	292
16.2.3	Problems with the Zinc Electrode	293
16.2.4	The Open Circuit Potential	295
16.2.5	Variation of the Potential During Discharge	295
16.3	Ambient Temperature Li/FeS ₂ Cells	296
16.4	Li/I ₂ Batteries for Heart Pacemakers	298
16.5	Lithium/Silver Vanadium Oxide Defibrillator Batteries	298
16.6	Zn/Air Cells	299
16.7	Li/CF _x Cells	303
16.8	Reserve Batteries	304
16.8.1	Introduction	304
16.8.2	The Li/SO ₂ System	304
16.8.3	The Li/SOCl ₂ System	306
16.8.4	Li/FeS ₂ Elevated Temperature Batteries	306
	References	307
17	Lead-Acid Batteries	309
17.1	Introduction	309
17.2	Basic Chemistry of the Pb-Acid System	310
17.2.1	Calculation of the MTSE	311
17.2.2	Variation of the Cell Voltage with the State of Charge	311

17.3	Potentials of the Individual Electrodes	312
17.4	Relation to the Mechanisms of the Electrochemical Reactions in the Electrodes	314
17.5	Construction of the Electrodes	314
17.5.1	Volume Changes and Shedding	316
17.6	Alloys Used in Electrode Grids	316
17.7	Alternative Grid Materials and Designs	318
17.8	Development of Sealed Pb-Acid batteries	318
17.9	Additional Design Variations	320
17.9.1	Other Improvements	322
17.10	Rapid Diffusion of Hydrogen in PbO ₂	322
	References	322
18	Negative Electrodes in Other Rechargeable Aqueous Systems	325
18.1	Introduction	325
18.2	The “Cadmium” Electrode	325
18.2.1	Introduction	325
18.2.2	Thermodynamic Relationships in the H-Cd-O System	326
18.2.3	Comments on the Mechanism of Operation of the Cadmium Electrode	327
18.3	Metal Hydride Electrodes	328
18.3.1	Introduction	328
18.3.2	Comments on the Development of Commercial Metal Hydride Electrode Batteries	328
18.3.3	Hydride Materials Currently Being Used	329
18.3.4	Pressure—Composition Relation	331
18.3.5	The Influence of Temperature	332
18.3.6	AB ₂ Alloys	335
18.3.7	General Comparison of These Two Structural Types	335
18.3.8	Other Alloys That Have Not Been Used in Commercial Batteries	336
18.3.9	Microencapsulation of Hydride Particles	336
18.3.10	Other Binders	336
18.3.11	Inclusion of a Solid Electrolyte in the Negative Electrode of Hydride Cells	337
18.3.12	Maximum Theoretical Capacities of Various Metal Hydrides	337
	References	338
19	Positive Electrodes in Other Aqueous Systems	339
19.1	Introduction	339
19.2	Manganese Dioxide Electrodes in Aqueous Systems	340
19.2.1	Introduction	340

	19.2.2	The Open Circuit Potential	341
	19.2.3	Variation of the Potential During Discharge	342
19.3		The “Nickel” Electrode	342
	19.3.1	Introduction	342
	19.3.2	Structural Aspects of the $Ni(OH)_2$ and $NiOOH$ Phases	343
	19.3.3	Mechanism of Operation	344
	19.3.4	Relations Between Electrochemical and Structural Features	346
	19.3.5	Self-Discharge	347
	19.3.6	Overcharge	349
	19.3.7	Relation to Thermodynamic Information	349
19.4		Cause of the Memory Effect in “Nickel” Electrodes	353
	19.4.1	Introduction	353
	19.4.2	Mechanistic Features of the Operation of the “Nickel” Electrode	354
	19.4.3	Overcharging Phenomena	356
		References	359
20		Negative Electrodes in Lithium Systems	361
	20.1	Introduction	361
	20.2	Elemental Lithium Electrodes	362
	20.2.1	Deposition at Unwanted Locations	362
	20.2.2	Shape Change	363
	20.2.3	Dendrites	363
	20.2.4	Filamentary Growth	363
	20.2.5	Thermal Runaway	364
	20.3	Alternatives to the Use of Elemental Lithium	365
	20.4	Lithium–Carbon Alloys	365
	20.4.1	Introduction	365
	20.4.2	Ideal Structure of Graphite Saturated with Lithium	367
	20.4.3	Variations in the Structure of Graphite	368
	20.4.4	Structural Aspects of Lithium Insertion into Graphitic Carbons	370
	20.4.5	Electrochemical Behavior of Lithium in Graphite	370
	20.4.6	Electrochemical Behavior of Lithium in Amorphous Carbons	372
	20.4.7	Lithium in Hydrogen-Containing Carbons	373
	20.5	Metallic Lithium Alloys	374
	20.5.1	Introduction	374
	20.5.2	Equilibrium Thermodynamic Properties of Binary Lithium Alloys	375
	20.5.3	Experiments at Ambient Temperature	375
	20.5.4	Liquid Binary Alloys	376

20.5.5	Mixed-Conductor Matrix Electrodes	377
20.5.6	Decreptitation	381
20.5.7	Modification of the Micro- and Nano-Structure of the Electrode	384
20.5.8	Formation of Amorphous Products at Ambient Temperatures	386
20.6	Protected Lithium Aqueous Electrolyte Systems	387
20.6.1	Introduction	387
	References	389
21	Positive Electrodes in Lithium Systems	391
21.1	Introduction	391
21.2	Insertion Reaction, Instead of Reconstitution Reaction, Electrodes	392
21.2.1	More Than One Type of Interstitial Site or More Than One Type of Redox Species	393
21.3	Cells Assembled in the Discharged State	393
21.4	Solid Positive Electrodes in Lithium Systems	395
21.4.1	Introduction	395
21.4.2	Influence of the Crystallographic Environment on the Potential	398
21.4.3	Oxides with Structures in Which the Oxygen Anions are in a Face-Centered Cubic Array	399
21.4.4	Materials in Which the Oxide Ions are in a Close-Packed Hexagonal Array	408
21.4.5	Materials Containing Fluoride Ions	412
21.4.6	Hybrid Ion Cells	412
21.4.7	Amorphization	413
21.4.8	The Oxygen Evolution Problem	414
21.4.9	Final Comments on This Topic	419
21.5	Hydrogen and Water in Positive Electrode Materials	420
21.5.1	Introduction	420
21.5.2	Ion Exchange	420
21.5.3	Simple Addition Methods	421
21.5.4	Thermodynamics of the Lithium: Hydrogen: Oxygen System	421
21.5.5	Examples of Phases Containing Lithium That Are Stable in Water	423
21.5.6	Materials That Have Potentials Above the Stability Window of Water	423
21.5.7	Absorption of Protons from Water Vapor in the Atmosphere	424
21.5.8	Extraction of Lithium from Aqueous Solutions	424
	References	424

22	Energy Storage for Medium- to Large-Scale Applications	427
22.1	Introduction	427
22.2	Utility Load Leveling, Peak Shaving, and Transients	428
22.3	Storage of Solar- and Wind-Generated Energy	428
22.4	Several Recent Developments That May Be Useful for These Applications	429
22.4.1	Hybrid Lead-Acid Batteries for Large Scale Storage	429
22.5	Batteries with Open Framework Crystal Structure Electrodes	432
22.5.1	Introduction	432
22.5.2	Insertion of Guest Species Into Materials with Transition Metal Oxide Bronze Structures	433
22.5.3	Materials with Cubic Structures Related to Rhenium Trioxide	434
22.5.4	Aqueous Batteries with Manganese Oxide Electrodes with Crystallographic Channels	434
22.6	Hexacyanometallate Electrode Materials	438
22.6.1	Introduction	438
22.6.2	The Structure of The Prussian Blues	438
22.6.3	Electrochemical Behavior of Prussian Blue	441
22.6.4	Various Cations Can Occupy the A Sites in the Prussian Blue Structure	444
22.6.5	Batteries with Prussian Blue Electrodes	444
22.6.6	Investigations of the Use of Polyvalent Prussian Blue Electrodes in Aqueous Systems	448
22.6.7	Work Toward the Commercialization of Aqueous Electrolyte Batteries Containing Prussian Blue Electrodes	448
22.6.8	Prussian Blue Electrodes in Organic Electrolytes	448
22.7	A New Class of Composite Anodes	451
22.8	An Alternative, Extension of the Stability Range of Aqueous Electrolytes	454
22.9	Batteries With Liquid Electrodes	457
22.10	Sodium/Sulfur Batteries	457
22.11	Flow Batteries	461
22.11.1	Introduction	461
22.11.2	Redox Reactions in the Vanadium/Vanadium System	463
22.11.3	Flow Batteries with a Modified Chemistry	466
22.12	All-Liquid Batteries	466
	References	469

23	Storage of Energy for Vehicle Propulsion	473
23.1	Introduction	473
23.2	ZEBRA Batteries	476
23.3	General Comments on Hybrid System Strategies	477
	References	478
24	A Look at the Future	479
24.1	Introduction	479
24.2	Emerging Technological Directions	480
24.3	Examples of Interesting New Research Directions	482
24.3.1	Organic <i>Plastic Crystal</i> Materials	482
24.3.2	Organic Electrode Materials for Lithium Batteries	482
24.3.3	New Materials Preparation and Cell Fabrication Methods	482
24.3.4	Batteries with Physically Moving Electrode Structures	483
24.3.5	Alternate Electrolytes	485
24.3.6	Interesting New High Power, Long Cycle Life Battery	485
24.4	Final Comments	489
	References	489
	Index	491