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Electrochemical Technologies for Energy Storage and Conversion

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1.1

Introduction

In this chapter, authors review the contemporary demand, challenges and future prospective of energy resources and discuss the relevant socioeconomical and environmental issues with their impact on global energy status. A sincere effort has been made to explore the better energy options of clean and sustainable energy sources such as hydro, biomass, wind, solar, geothermal, and biofuel as an alternative to the conventional energy sources. Electrolysis, photoelectrochemical, and photocatalytic water-splitting techniques were adopted for green and light fuel generation. Advancement in electrochemical technology for energy storage and conversion devices such as rechargeable batteries, supercapacitors, and fuel cells are also briefed.

1.2

Global Energy Status: Demands, Challenges, and Future Perspectives

World's economy revolves around the axis of energy prices, which are primarily governed by the political consequences, environmental impact, social acceptance, availability, and demand. Nation-wise world's energy consumption plot (1980–2050) is depicted in Figure 1.1, which rated the United States, China, Russia, South Korea, and India as potential energy consumers. Energy consumption rate of our planet in 2007 was 16%, which would be accelerated to an alarming rate of 34% by 2050 (Figure 1.2) [1]. Our severe dependency on oil and electricity makes energy a vital component of our daily life [2]. Soaring prices of oil (starting from \$42 per barrel in 2008 to \$79 per barrel in 2010, to \$108 per barrel in 2020 and \$133 per barrel in 2035) as projected in Figure 1.3 [3] and other associated necessary commodities along various burning environmental issues resulted from industrial revolution compel us to give a careful thought on this serious issue. Figure 1.4 assesses the geographical region-wise oil reserve that projects the oil assets and capacities of the different regions [4]. The current global energy scenario

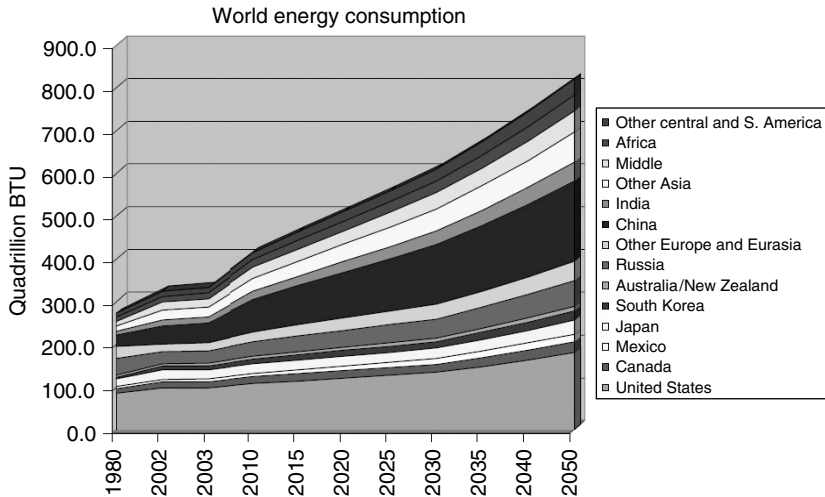


Figure 1.1 Nation-wise world energy consumption in the time interval of 1980–2050. (Energy Information Administration Annual Energy Review, 2007.)

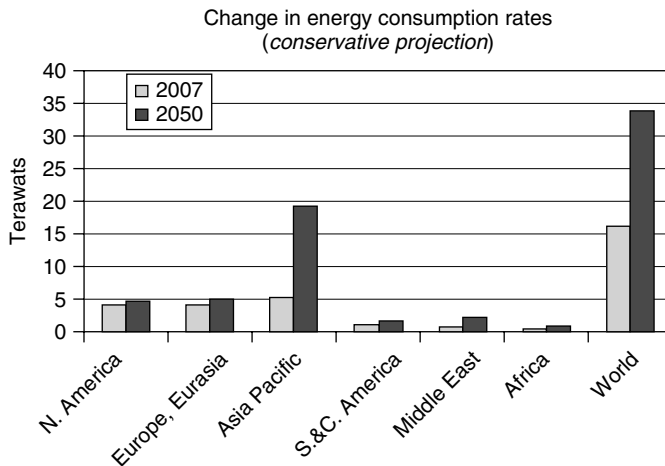


Figure 1.2 Comparative change in energy consumption rates of different zones against the world (actual reported for 2007 vs projected for 2050). (Renewable in global energy supply: an IEA fact sheet, January 2007.)

is full of uncertainty and faces three major energy challenges in the form of energy demand/energy supply ratio and security and their impact on the environment. The present worldwide population of 6.9 billion needs 14 TW annual energy [5] to sustain the current standard of life. Of the total energy production, 45% is required for industries, 30% for transport, 20% for residential and commercial buildings,

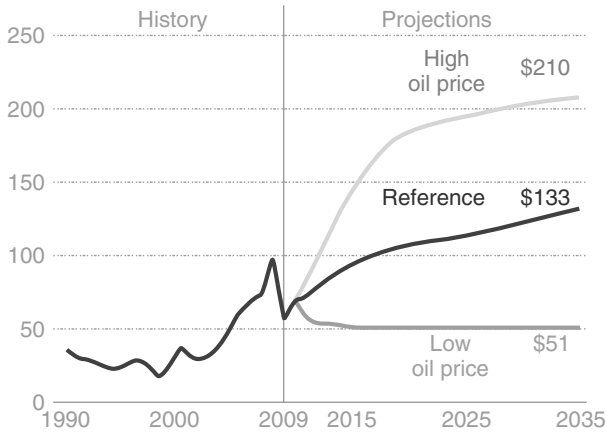


Figure 1.3 World oil prices in three oil price cases on the timescale of 1990–2035 (\$2007 per barrel). (1980–2035: EIA, Annual Energy Outlook 2010, DOE/EIA-0383(2010) (Washington, DC, April 2010), web site: www.eia.gov/oiaf/aeo.)

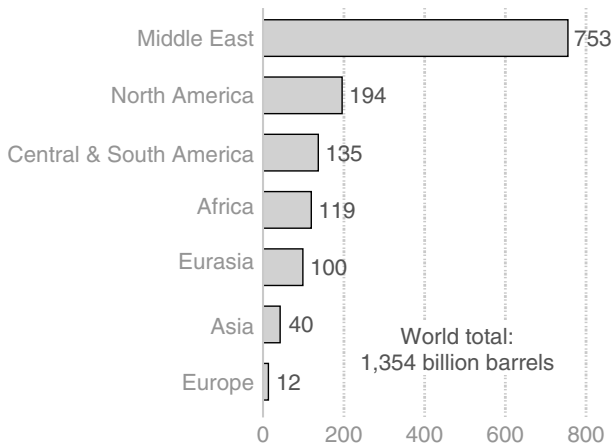


Figure 1.4 World's proved oil reserves by geographic region as of 1 January 2010 [4].

and the rest for services such as education, health, finance, government, and social services. Electricity is the world's fastest growing form of end-user energy consumption. Coal provides the largest share in the world's electricity generation, accounting for 42% in 2007, and its share will be largely unchanged through 2035. Rest share of the world's electricity generation is contributed by water, natural gas, nuclear power, hydropower, wind, and solar power. Economic trends and population growth drive the commercial sector activities and the resulting energy use.

The need for services (health, educational, financial, and governmental) increases as population increases. Slower expansion of gross domestic product (GDP) and declining population growth rate in many organization for economic cooperation and development (OECD membership) nations contribute to slower anticipated rates of increase in commercial energy demand. In addition, continued efficiency improvements moderate the growth of energy demand over time, as energy-using equipment is replaced with newer and more efficient stock. World's projected population would be quadrupled by 2050, the energy use doubled and electricity consumption tripled to our present energy demand. According to Hubbert's bell-shaped curve [6] of the worldwide oil production projection, we have already attained the peak and now observe a downfall and finally, the oil will last for 200 years (Figure 1.5) [7]. Lord Ron Oxburgh, former chairman of Shell, gave the statement on oil production possibilities and price, "It is pretty clear that there is not much chance of finding any significant quantity of new cheap oil. Any new or unconventional oil is going to be expensive." Despite the greenhouse gas concentrations approaching twice as those in the preindustrial period, coal and gasoline are still the major energy sources (34.3% oil, 25.9% coal, 20.9% gas, 13.1% renewables (10.4% combustion renewables and waste, 2.2% hydro, and 1.5% other renewables). Furthermore, alternative sustainable energy sources are still in the experimental stage; for example, some recent studies suggest that biofuels may not be as effective in reducing greenhouse gas emissions as previously thought. As a result, many countries have relaxed or postponed renewal of their mandates [8]. For example, Germany reduced its biofuel quota for 2009 from 6.25 to 5.25%. Therefore, governments, industrialists, and researchers have put their heads together on this leading energy issue with their concerns about the environmental challenges and renewed

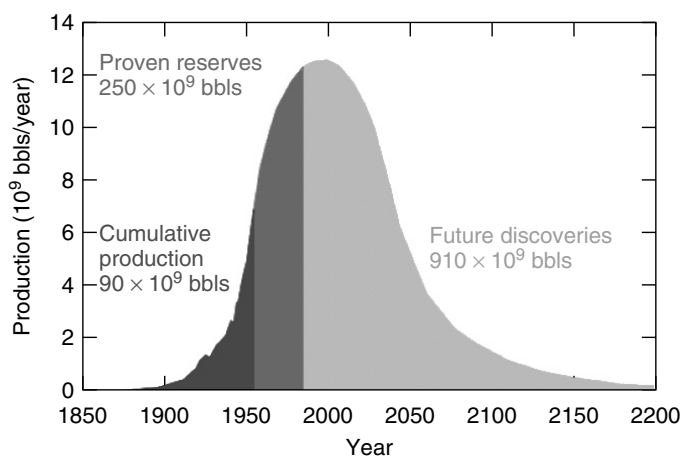


Figure 1.5 Hubbert's bell-shaped curve for time versus production of any exhaustible resources projection plot for the time interval 1850–2200 AC [7].

the interest in development of alternatives to fossil fuels, specifically, nuclear power, and renewable energy sources (wind, solar, biofuel, geothermal, tidal, hydro) using breakthrough concepts (catalysis by design, multielectron transfer) and accelerated application of cutting-edge scientific, engineering, and analytical tools. There are three major options of getting clean energy including carbon neutral energy (fossil fuel in conjunction with carbon sequestration), nuclear, and renewable energy. To satisfy the 10 TW no-carbon energy demands [9], a 38% conservation of energy for the next 50 years via combustion of fossil fuel is required, but the challenge of disposing 25 billion metric ton of CO₂ annually needs to be conquered. The need for nuclear-powered energy required the establishment of 365 GW electric nuclear fission plants per year for 50 years. The amount of annual renewable trappable energy from resources is as follows: the most viable and abundantly sourced solar energy with a capacity of 12 000 TW; integrated overall geothermal energy, 12 TW; globally extractable wind power, 2–4 TW; tidal/ocean current, 2 TW; and hydroelectric energy, 0.5 TW. Among all sources, obviously solar energy stands out as a promising choice of renewable energy, and currently, we are exploiting it only for the satisfaction of 0.1% of the demand. Therefore, by reducing energy demand and emissions accompanied with the use of the diversifying energy sources, we should be able to meet our energy target.

1.3

Driving Forces behind Clean and Sustainable Energy Sources

Our atmosphere is in a constant state of turmoil, and it is never being static. Relatively, internal and external changes in the earth's atmosphere, made by either Nature or man, bring changes in weather and climate. Scientific evidences pointed out the role of man in environmental degradation by insanely exploiting Mother Nature, which causes a disturbance in the delicate balance of Nature by accelerating global warming and associated climate changes, increasing ocean temperature, and bringing out changes in terrestrial geography, rain fall ratio, temperature, and type of soil. These changes fuel the growing consensus about the eminent need for a more pervasive action for environmental protection. Technological advancement attained during the past two decades has provided us a comfortable lifestyle full of facilities on a very high cost of resources consumption and degradation of our environment. The effect of the world's economic development on the environment was defined in the words of Elsa Reichmanis, the former president of the American Chemical Society, "We are past the days when we can trade environmental contamination for economical prosperity that is only a temporary bargain and the cost of pollution both economically and on human health is too high" [10]. However, it has disturbed ecological balance and damaged the environment, which has been proven disastrous for global life and has resulted in tremendous critical issues such as extinction of rare species of flora and fauna from earth, various incurable or semicurable diseases, global warming, acid rain, ozone layer depletion, excessive pollution, nuclear winter, and photochemical smog, especially

in and around the urban areas. But still we do not wish to quit the comfortable lifestyle, and we simply cannot afford to continue along this path. Therefore, it is high time we shake hands with Nature to satisfy our energy demands in an eco-friendly manner by utilizing decentralized renewable energy sources such as solar power, wind, geothermal energy, biofuel and biomass, tidal power, wave, and hydropower. Furthermore, these sources are more efficient, abundant, and affordable (available free of cost) and are an environmentally benign solution for getting clean and green energy but on the condition that people master the technology. Both industrialized and developing countries should adopt the above-mentioned sustainable resources to build their energy capacity and improve their regulatory for clean, safe, and renewable energy. Therefore, large-scale transformation in energy policies should be executed with strong willpower along the necessary course of action toward clean and sustainable energy. Volatile energy prices of fossil fuels and increasingly scarce natural resources impend the government legislation that a growing trend of higher corporate social responsibility (CSR) and consumer sentiment favor environmentally friendly products and services. They induce the businesses, industries, and governments to respond in the innovative ways that might have been unimaginable just a few years ago. Executing relatively new wireless technology, networked sensors, management dashboard reporting, and automated alarm management is one way for businesses to reduce waste and optimize their position as environmental stewards in multiple domains (company, government, and geography). Reducing waste, managing scarce natural resources, saving energy, and following efficient operating conditions have always been good business tenets. The vital driving force behind the search for the most powerful, clean, and renewable energy sources is energy security for the future in energy policies of the governments all around the world, assuming renewable energy sources as a *guaranteed growth sector* [11]. Modern renewable energy industry has been hailed by many analysts because of the global trends and drivers underlying its expansion during the past decade. Without widespread improvements in environmental stewardship, impacts from the fundamental drivers will lead to adverse consequences around the world. Among these consequences, strict government legislations, climate changes, water stress, natural resource and raw material scarcity, public pressure, market risk and national security, and safety concerns are highlighted below.

1.3.1

Local Governmental Policies as a Potential Thrust

In 1960s, the slogan *Think Globally and act Locally* was coined by David Ross Brower, a prominent environmentalist and the founder of Sierra Club Foundation, John Muir Institute for Environmental Studies, and Friends of the Earth (1969), and many others that work actively for environment and initiate the worldwide consensus and awareness about environmental issues. In many countries, great progress has been made through awareness programs, proactive guiding principles and policies, new legislation, and government incentives in the form of tax relaxation

and subsidies. Environmental risks force the people to go green in a significant way and promote a joint effort at governmental, enterprise, and even individual level to contribute in the awareness programs, proactive guiding principles, and policy making, all together. Government policies for renewable energy are a diverse and growing segment. Hundreds of local governments are setting future targets and adopting a broad array of proactive planning and promotion policies, including new legislation, government incentives for local feed-in tariffs and renewable electricity generation and heating, and mandates for buildings and businesses. Government regulations can play an efficient role in achieving effective changes in favor of environment, but it's only one out of several forces that will drive the needful changes into the future.

1.3.2

Greenhouse Gases Emission and the Associated Climate Changes

Emission of greenhouse gases significantly banks on industries, refrigeration, and transportation because fossil fuels, which are still a primary energy source and responsible for CO₂ emission, are accounted as one of the greenhouse gas. Major driving forces and science behind the *green* movement are focusing primarily on suppressing greenhouse gas emissions and their unwanted effects on global warming and associated climate changes, natural resource scarcity (oil, gasoline, and minerals in particular), and eventual ozone layer depletion, consequences of unabated human-driven pollution. New legislation, community pressure, customer safety concerns encourage proactive actions and strengthen the corporate environmental activities. Environmental improvement is one area of new business activity whose driving forces are so strong, responsibly compelling, and widely appreciated that raise the call to action and can appeal to every industry, enterprise, and organization, from the senior-most executives to the newest entry-level employees.

1.3.3

Public Awareness about Environmental Protection Rose around the World

Baton of the public awareness lights the world to see the real picture of mesmerization of environment done by humans, which push the government and industries to enact on the holistic green strategies to make this world more livable. Layman protesting by chaining themselves to trees or lying in front of bulldozers against deforestation and by organizing boycotts are the most visible environmental stewardships in 1980–1990s against the activities of *big business*, which enforce driving forces behind environmental sustainability. But nowadays the clashes between the corporate world and the environmentalists have become a thing of past. Businesses are adapting and applying suitable methodology to sustain the benefits to business operations without going against Nature. Moreover, they started working in favor of Nature by cross-company, cross-industry, and cross-geography cooperation, which will enable a clear and sustainable focus on

improving environment by applying technology in new ways to achieve granular understanding of their operation and their impact on the planet. Public who wants to ride on green wings becomes a major positive driving force for environmental protection. However, public pressure could shift from a positive driving force to a more negative one. Public pressure in the form of unrest is certainly more likely when food production declines while population rises, basic natural resources become scarce, water supplies become more stressed, and there is occurrence of more frequent and more severe natural disasters. Public sympathy is also with endangered species of flora and fauna, an important part of the food chain that might perish because of global warming and associated climate changes. One survey on average American attitude toward the environment found out that more than three-quarter US workers want to have an employer, who is well informed about green movement on a daily basis and contributes accordingly [12]. Furthermore, developments in renewable energy have enough potential to create new industries and generate millions of new jobs around the world. The European Commission published statistics on Europeans' attitudes toward climate change and found that 73% of the Brits feel they were well informed about the causes of climate change and methods to tackle them, placing them in the same group as the citizens of Sweden, the Netherlands, and Finland. Despite all this, only 46% Brits and 50% Europeans but 82% Swedish ranked climate change as the most alarming global problem.

1.3.4

Population Growth and Industrialization

World population continues to grow, and statistical analysis predicts that by the year 2050, it will be increased by 30% of today's population, which will accelerate scarcity of natural resources such as oil, fossil fuel, water, minerals, agricultural land, and clean air. Industrialization further demands additional resources that can create environmental risk and jeopardizes the economy. The Intergovernmental Panel on Climate Change (IPCC) reported in 2007 [13] that the future climate change attributable to global warming is expected to put 50 million extra people at risk of hunger by 2020, which might be increased to 132 and 266 million by 2050 and 2080, respectively, because rising air temperatures could decrease rain-fed rice yields by 5–12% only in China and net cereal production in South Asian countries could decline by 4–10% by the end of this century, making it unable to meet the food demands of that time. Pressure of high consumption of resources because of population explosion, requiring more amount of drinkable water without drought or climate change. Furthermore, the threats such as oil and chemical spills, unmitigated waste, resources exploitation, residential and commercial real estate development, unsafe living conditions, and drainage of polluted industrial waste into river system pose a clear risk to public health and degrade the environment, enhancing the ultimate depletion or extreme scarcity, which would generate high risk to business and Nature.

1.3.5

Security and Safety Concerns Arising from Scarcity of Resources

National security became more relevant when the impact of climate or weather change crosses the country borders and countries rich in natural resources start dominating other countries. Public unrest develops as resource supplies become scarce and global conditions become adverse enough to result in riots, corruption, and military action and is a sufficient cause for disturbing national or international security. Safety for all living organisms and properties is another issue that prominently arises after any natural disaster, which is a result of global warming and associated climate changes, such as severe weather patterns, floods, fires, and hurricanes. Generous cooperation in the form of human help and financial support among countries with proactive measurements can make the affected country or region to be able to overcome the situation effectively. The above-mentioned risks are also a driving force behind environmental protection to mitigate before any of the direst predictions unfold and the current course of global cooperation changes.

1.3.6

Platforms Advocating in Favor of Sustainable and Renewable Resources

Environmental degradation, soaring prices and high consumption of conventional energy sources, perpetual resource wars, catastrophic effect of greenhouse gases on climate change, inextricable link between nuclear weapons and nuclear power, high cost of nuclear plant establishment and nuclear fuel, and problematic disposal of nuclear waste have fostered the international agencies to establish a platform such as United Nations Environmental Program (UNEP) that advocates renewable energy sources to take the place of fossil fuels without resorting to nuclear-powered energy. In 2000, a global network for the elimination of nuclear weapons lobbied nations (accounted 142 in 2009) around the world to institute the International Renewable Energy Agency (IRENA). IRENA opened its headquarters in Abu Dhabi and branch offices in Bonn and Vienna, and it is committed to becoming a principal driving force in promoting a rapid transition toward the sustainable use of renewable energy on a global scale. It included all forms of renewable energy produced in a sustainable manner, including solar power, wind, geothermal energy, hydropower, ocean, and appropriate bioenergy. Another example of such agencies is the Forest Stewardship Council (FSC) certifies some wood as sustainable when it meets the established criteria [14]. The U.S. Green Building Council (USGBC) has created the Leadership in Energy and Environmental Design (LEED, founded in 1993 by Robert K. Watson), a third-party certification program for the design, construction, and operation of green buildings. All agencies working together under the same theme to benefit the environment are a positive driving force.

1.3.7

Economic Risk Generated from Price Pressure of Natural Resources

World economy is a grand driving force to regulate the energy and raw material prices. Speculation on long-term demand, current availability, and cost of resources suggest some substitute raw materials, alternative or renewable energy sources, and conservation of traditional fossil fuels. As long as energy and commodity prices for scarce raw materials remain unpredictable and long-term global demand sustains the heightened levels, the drive for initiatives that reduce energy consumption and raw materials waste or shift to a less risky source with a more stable long-term cost has become stronger. For example, in 2004, crude oil was trading at \$40 a barrel and the estimated *fair value* was to be only \$27 a barrel [15]. Risk premium has varied up to 30% and potentially higher over time. On the other hand, the price for water in many areas of the world is still much lower than its actual economic value, which is a notable exception for water management. Price pressure alone is a powerful driving force, and as result of this, the world would be destined to experience an endless ebb and flow of cyclical activity without new taxation or *cap-and-trade* mechanisms to sustain the current green movement. That's why some enterprises install straightforward technology devices, such as motion-sensitive light switches, implement new technology to monitor and optimize energy consumption, train employees on energy-saving practices, or appoint new roles in the organization with accountability for achieving business and environmental benefits.

1.3.8

Regulatory Risk from Governmental Action and Legislation

Regulatory risk from new governmental legislations and global agreements is a powerful driving force that can accelerate the trend of environmental sustainability if applied effectively. The United Nations held a conference in 1997 at Kyoto, Japan, on climate change that resulted in an international agreement. The Kyoto Protocol took effect from 2005 to reduce greenhouse gas emissions worldwide, but the protocol's obligations are limited to monitoring and reporting, without actual provisions for enforcement and penalties if reductions are not achieved. Another prominent meeting of leading industrial nations (G8) held at Tokyo, Japan, 8 July 2008, endorsed halving world emissions of greenhouse gases by 2050 but set no near-term targets. The UK Climate Change Act (2008) aims to move the United Kingdom to a low-carbon economy and society, with an 80% cut in emissions by 2050 from a 1990 baseline [16]. The California Energy Commission recognizes the energy efficiency standards for real estate business and made future legislation that would require zero net energy homes and commercial buildings by 2020 and 2050, respectively [17]. In this series, the U.S. Army Energy Strategy set five tenets in 2005 to the strategy: eliminate waste, increase efficiency, reduce dependence on fossil fuels, conserve water resources, and increase energy security. Regulatory proposals being actively developed at the industrial, state, and local levels are more

effective than the legislations at global and country levels. Therefore, it is high time for nations to follow international regulations strictly.

1.3.9

Fear of Reputational Risk to Strengthen Corporate Social Responsibility

Reputational risk at CSR is a vital driving force for companies to improve their status as environmental friendly, and it is viewed as an investment that brings financial returns and an opportunity or platform for growth that would increase the visibility in action. To reduce environmental impact, businesses adopted ethical standards to win customers' loyalty and market share and lowered their business risk that led to higher profitability through increased sales or decreased costs, which were often maintained during the adverse environmental events. A large number of companies are enrolled under the CSR network and few of them are (i) Catalyst Paper Corporation (Canadian) uses its own by-products (biomass) to power its operations; (ii) Tesco is a retail chain holder in grocery and industries (>2800 stores in central Europe, Asia, and North America), runs 75% of its delivery fleet on biodiesel fuel, had labeled 70 000 of its products with carbon counts (carbon labeling articulates the total carbon emissions from bringing a product to the store shelf) by 2008, and runs many straw-powered stores with heat and solar photovoltaic (PV) power plant for carbon-neutral electricity; and (iii) Wal-Mart (Latin America) has installed the largest sun-operated PV installation to satisfy 20% of the energy needs of its store. In California, new cars being sold are required to include labeling with *global warming scores*.

1.3.10

Operational and Supply Chain Risks from Inefficiencies and Environmental Changes

Operational and supply chain risks are another driving force generated from extreme adverse weather patterns, environmental hazards, and inefficiencies that will push the businesses to invest in innovative and sustainable energy sources and high-impact renewables, to favor upstream suppliers, and to set examples for other business partners. Although opportunities have been available since the past decades, only recently have all the driving forces aligned in the right direction to prompt the worldwide call to action.

1.4

Green and Sustainable Energy Sources and Their Conversion: Hydro, Biomass, Wind, Solar, Geothermal, and Biofuel

Environmental degradation and soaring prices and high consumption of conventional energy sources (34.3% oil, 25.9% coal, 20.9% gas, 13.1% renewables (10.4% combustion renewable and waste, 2.2% hydro, and 0.5% other renewables),

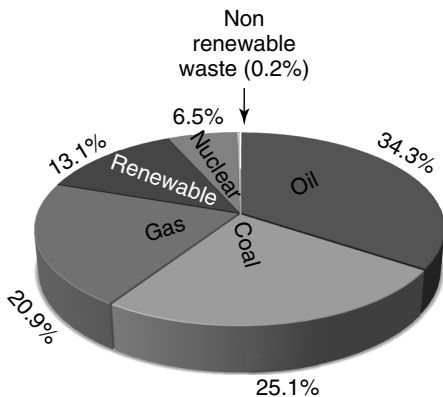


Figure 1.6 World total energy (conventional and renewable) consumption plotted against their percentage contribution (total primary energy, 410 EJ/year) (http://www.iea.org/papers/2006/renewable_factsheet.pdf).

6.5% nuclear, and 0.2% nonrenewables) are illustrated in the world energy consumption chart (Figure 1.6). The perpetual resource wars, catastrophic effect of greenhouse gases on climate change, inextricable link between nuclear weapons and nuclear power, high cost of nuclear plant establishment and nuclear fuel, and problematic disposal of nuclear waste all foster the international agencies to develop the sustainable energy sources to take the place of conventional energy sources without resorting to nuclear power. All time free availability and huge amount of decentralized renewable energy are the principal driving force against the promotion and rapid transition toward the sustainable renewable energy on the global scale. Renewable energy includes a wide spectrum of sustainable and powerful sources of natural energy such as solar, wind, geothermal, hydropower, ocean, and appropriate bioenergy. One can estimate the power of these sources as a single day of sunlight can supply enough energy to satisfy the world's electricity demand for 8 years, whereas wind can meet the world's electricity needs 40 times over and is capable of fulfilling all the global energy demands five times over, and the geothermal energy stored in the top 6 miles of the earth's crust contains 50 000 times the world's energy storage in oil and gas resources. Tidal, wave, and small hydropower can also provide vast stores of energy, available everywhere on earth. Both industrialized and developing countries should start adopting the above-mentioned sustainable resources to build their energy capacity and improve their regulatory for clean, safe, and renewable energy. By the year 2008, the top six countries rated by their total amount of renewable power capacity in use were China (76 GW), US (40 GW), Germany (34 GW), Spain (22 GW), India (13 GW), and Japan (8 GW) (9 September 2009, by Eric Martinot and Janet Sawin, London, UK, Renewables Global Status Report 2009 and update of the Renewable Energy Policy Network for 21st Century (REN21) annual report). Renewable energy capacity in developing countries grew to 119 GW in 2009, or a 43% share (out of which, 18% is

Table 1.1 Renewable energy added and existing capabilities, 2008 (estimated).

	Added during 2008	Existing at the end of 2008
Power generation (GW) electric		
Large hydro power	25–30	860
Wind power	27	121
Small hydro power	6–8	85
Biomass power	2	52
Solar PV grid connected	5.4	13
Geothermal	0.4	10
Concentrating solar power	0.06	0.5
Ocean (tidal) power	0	0.3
Hot water or heating (GW) (thermal)		
Biomass heating	n/a	250
Solar for hot water/space heating	19	145
Geothermal heating	n/a	50
Transport fuels (billion liters/year)		
Ethanol production	17	67
Biodiesel production	3	12

Global Energy Report-2009 REN21.

global electricity supply) of the total global energy capacity. Even though affected by the global economic downturn, the years 2008 and 2009 were remarkably the best for renewable, which is clear from Table 1.1, exhibiting the existing sources, and by 2008, renewable energy was added. The Global Status Report of 2010 on renewables conducted by REN21 shows that all the forms of grid-tied solar PV plants grew annually by 60% from the past decade. On average, the past 5 years' annual growth of wind power was 27%, solar hot water was 19%, and the ethanol and biodiesel production expanded by 34% [18]. Heat and power from biomass and geothermal sources continued to grow, and small hydropower increased by 8%. Globally, the approximate technology share of \$120 billion (€85 billion) as renewable capital investment was divided into wind power (42%), solar PV (32%), biofuels (13%), biomass and geothermal power (6%), solar hot water (6%), and small hydropower (5%). Renewable capacity is discussed individually in the following sections.

1.4.1

Solar PV Plants

PV power generation employs solar panels comprising a number of cells containing a PV material, which include monocrystalline silicon, polycrystalline silicon, amorphous silicon, cadmium telluride, and copper indium selenide/sulfide. The cost of PV's has declined steadily since the first solar cells were manufactured, because of the advancement in technology and large-scale manufacturing units

[19]. More than 1800 solar PV plants of 16 GW existed worldwide by the end of 2008; Spain was leading with 2.6 GW of new capacity added, followed by the former PV leader Germany (added 1.5 GW), the United States (310 MW added), South Korea (200–270 MW), Japan (240 MW), and Italy (200–300 MW). Solar PV markets in Australia, Canada, China, France, and India have also continued to grow. Their additions reached a record high of 7 GW in 2009, when Germany topped the market with 3.8 GW added capacity and captured more than half of the global market. Other large markets were Italy, Japan, the United States, Czech Republic, and Belgium.

1.4.2

Wind Power

Wind power is the conversion of wind energy into a useful form of energy, such as using wind turbines to make electricity, wind mills for mechanical power, wind pumps for pumping water or drainage, and sails to propel ships. Around the world, >80 countries had installed commercial wind power by the year 2008 for their energy demand. The global wind power leader since mid-1990s, Germany (24 GW), has handed over its top position to the United States (25 GW), followed by Spain (18 GW), China (12 GW), and India (8 GW). Wind power additions reached a record high of 38 GW, that is, around 60% of the total global energy capacity (80 GW) on renewables utility scale investment in 2009 (excluding small projects). China tops the market with 13.8 GW, the United States was second, with 10 GW added. The share of wind power generation in several countries reached record highs, including 6.5% in Germany and 4% in Spain.

1.4.3

Geothermal Power

Geothermal wells release greenhouse gases trapped deep within the earth, but these emissions yield much lower energy per unit than those of fossil fuels. As a result, geothermal power has the potential to help mitigate global warming if widely deployed in place of fossil fuels. The United States remained the world leader in geothermal power development, with more than 120 projects underdevelopment, representing at least 5 GW. Geothermal projects were underway in over 40 countries, with another 3 GW in the pipeline. Globally, geothermal power capacity reached over 10 GW in 2008 and is increasing yearly [20].

1.4.4

Concentrating Solar Thermal Power (CSP) Plants

Concentrating solar thermal power (CSP) plants employ sunlight concentrated onto PV surfaces for the purpose of electrical power production. The United States and Spain are the leading figures in this field. New projects are also underdevelopment in Abu Dhabi, Algeria, Egypt, Israel, Italy, Portugal, Spain, and Morocco. One

of the key trends is that a growing number of these CSP plants will include thermal storage in daytime, allowing power generation in the evening hours. The recently completed Andasol 1 plant in Spain has more than 7 h of full-load thermal storage capability. Overall, it is clear that parabolic trough plants are the most economic, most mature, and efficient thermal storage plants and a promise to solar thermal technology available today, although there are still significant areas for improvement and cost cutting in the near future.

1.4.5

Biomass

Biomass production contributes the energy equivalent of 5% of world gasoline output. Many countries evident the record use of biomass, notably, Sweden, where biomass accounted for a larger share of energy supply than oil for the first time in 2009, which was followed by Brazil.

1.4.6

Biofuel

The United States scored top in biofuels with 31 new ethanol refineries of 40 billion l per year production strength along with an additional 8 billion l per year capacity under-construction plants established by the year 2009. In transport fuels, ethanol production in Brazil ramped up dramatically in 2008 to 27 billion l in 400 ethanol mills and 60 biodiesel mills, after being maintained constant for a number of years, for the first time ever; more than half of Brazilian nondiesel vehicle fuel consumption came from ethanol. Notwithstanding Brazil's achievement, the United States remained the leading ethanol producer, with 34 billion l produced in 2008. Other ethanol fuel-producing countries include Australia, Canada, China, Colombia, Costa Rica, Cuba, the Dominican Republic, France, Germany, India, Jamaica, Malawi, Poland, South Africa, Spain, Sweden, Thailand, and Zambia. The European Union (EU) alone is responsible for about two-thirds of world biodiesel production, with Germany, France, Italy, and Spain with a biodiesel production capacity of 16 billion l per year in more than 200 biodiesel production units, and an additional ethanol production plant with a capacity of over 3 billion l per year is under construction.

1.5

Electrochemistry: a Technological Overview

Electrochemistry serves to illustrate the fundamentals related to the existence and movement of electrons present in bulk, as well as the interfaces between ionics, electronics, semiconductors, photonics, and dielectric materials and their consequences on various fields of science, that is, chemistry, engineering, biology, materials, and environmental [21–23]. It also accomplishes the reverse of above,

that is, withdrawal of electricity from energetic chemicals by electrolysis. Electrons are inexpensive redox reagents, as the cost of a mole of electrons is <\$0.01 compared to \$0.03–\$3.00 for common redox reagents [24]. John O'M Bockris described electrochemistry as a subject that deals with the making of substances by means of electricity or making of electricity by consuming substances. In traditional electrolytic techniques, the electric current directly passes between the electrodes (anode and cathode) in contact with the electrolytic phase that contains ions. Since 1972 [25], when the use of semiconductor materials as electrodes came into much closer focus, it widely extended the realm of subjects that can be treated under electrochemistry. Electrodes (anode and cathode) bring about specific chemical changes (oxidation and reduction, respectively), usually in conditions close to ambient temperature and pressure, without the use of any toxic reagents. Electrolysis can be a selective, an easily computer controllable, a convenient, and a cost-effective technology for synthesis, separation, characterization, and pollution control. Sophisticated electrochemical cells and cell components are readily available in market to assist us with high technical expertise. Suitable electrolytic cells are available off the shelf and are capable of being combined with other necessary processor units to construct fully integrated and compact production systems, which may be in a batch or continuous process. Electrochemical phenomenon plays a fundamental role in providing essential materials and devices that contribute significantly to the area of importance in national security and well-being of the mankind. Moreover, humans themselves are bioelectrochemical machines, converting solar energy stored in food via electrochemical reaction into muscle power. On the basis of widely spread occurrence of the electrolytic phenomenon in technology and devices, the arena of electrochemistry is categorized as follows:

- **Materials** of interest includes concrete, ceramic, catalytic materials, composites, colloids, semiconductors, surfactants, inhibitors, biomaterials such as proteins and enzymes, emulsion and foams, metal and alloys, ionic solids, dielectric, polymers, membrane and coating, and aqueous and nonaqueous solvent solutions.
- **Phenomena** that arise in the materials include conduction process, mass transfer by convection, ion exchange, potential field effect, adsorption, electron and ion disorders, colloidal and interfacial activity, wetting, membrane transport, sintering, dendrite formation, electrokinetics, electrocatalysis, passivity, bubbles evolution, and gaseous discharge (plasma) effect.
- **Processes** that critically depend on phenomenon include energy conversion and storage, chlor-alkali industry, pulp and paper, corrosion and corrosion control, membrane separation, surface reactions, desalination, deposition and etching by electrolytic and plasma processes, mining and metallurgy, environmental protection and control, water and wastewater treatment, processing and fabrication, electrochemical synthesis of inorganic and organic chemicals, and pollution detoxification and recovery.
- **Products** resulting from these processes include batteries and fuel cells, microelectronic devices, devices in information technology, ceramics, sensors, membranes, metals, gases, coatings and films, chemicals, pharmaceuticals, and microelectronics

This multidisciplinary field identifies new technological opportunities in widely diverse applications and underpins many technologies. In addition, cutting-edge applications in new areas, including *in situ* characterization, interfacial structures, surface reactions, and plasma, also hold great promise for advancement in the field. Aluminum for building and aircraft and titanium for supersonic aircraft and tanks are made of electrochemical processes. Highly sensitive microsensors implanted in human body can precisely report about the biochemical changes in the body. Electrochemical knowledge has been made feasible to accelerate the healing of tissue and to simulate the action of nerves that have been damaged. Electrochemical life-lasting batteries for pacemakers are also available in market. Coatings for car that would not change in appearance after years of service along with propulsion system for electric vehicles and methods to remove toxic materials selectively from streams of waters have also been made available. The electronics industry underwent a rapid evolution from thick to thin films during the last decade and often played an important and decisive role in the plating through mask technology, plating for thin film heads, plating for high density magnetic thin film, selective etching technology, and so on. New electrochemical approaches have also been playing the prominent roles in the electronics industry, and their activities touch almost all industrial sectors.

While all these technologies are based on the same fundamental principles but their practical manifestations may be quite different with, for example, cell configurations, electrode materials and sizes, electrolytes and separators, each designed to meet the particular demands of the application. Electrolysis should be selected as the preferred method over other competitive chemical routes because redox species are always recycled; hence, only small amounts of redox reagents are used without any stoichiometric by-products. High solubility of reactants required for viable current density is a major limitation of electrochemical technology.

1.6

Electrochemical Rechargeable Batteries and Supercapacitors (Li Ion Batteries, Lead-Acid Batteries, NiMH Batteries, Zinc–Air Batteries, Liquid Redox Batteries)

Electrochemical rechargeable batteries or secondary batteries [26] are energy storage devices, receive electricity that is produced elsewhere, and utilize electricity to derive electrochemical reactions (uphill, a positive ΔG) at both electrodes and become ready to release this energy downhill in a spontaneous manner. A handsome variety of rechargeable batteries is available in commercial market (including lead-acid, nickel cadmium (Ni-Cd), nickel metal hydride (Ni-MH), zinc–air, liquid redox, lithium ion (Li ion), and lithium ion polymer batteries) (Figure 1.7); they come in different shapes and sizes with different energy to weight and energy to volume ratios connected to stabilize an electrical distribution network and can be used several times. Batteries are good at providing high power levels, but the amount of energy they can store per unit weight ($50\text{--}1000\text{ W kg}^{-1}$) is not greater

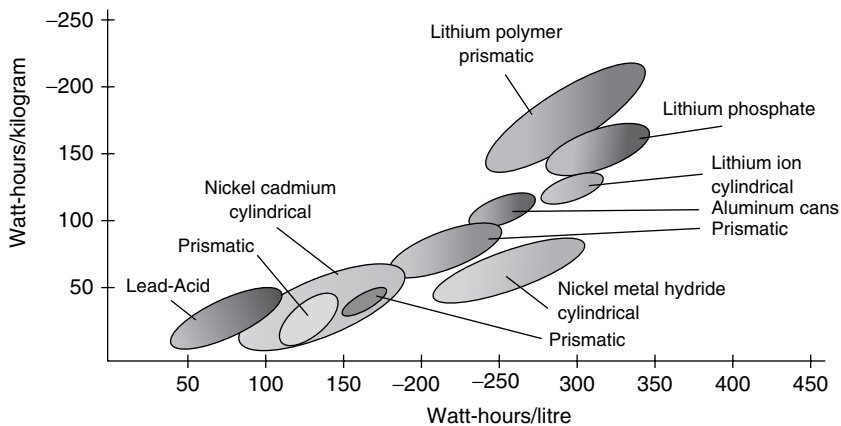


Figure 1.7 Different kinds of batteries rated on the scale of their energy to weight and energy to volume ratios. (http://en.wikipedia.org/wiki/Rechargeable_battery).

than that of fuel cells because they can use up, at best, all the material on their plates, whereas fuel cells simply convert all the available chemical fuel into energy. Most of the present day rechargeable batteries have to be cycled about 100 times when the depth of discharge (DOD) is 90%; moreover, the batteries beyond 1000 recharges with a high DOD are also available. Furthermore, the systems with 50 000 recharges are possible at a 40% DOD. The calendar life of batteries depends on their mode of use. They have made a revolutionary impact on our lives; for example, they can be used in applications such as automobile starters, portable consumer devices, light vehicles (such as motorized wheelchairs, golf carts, electric bicycles, and electric forklifts), tools, providing long-term power to internal artificial organs (heart pace makers, hearing aids, etc.), and providing uninterruptible power supplies. Grid energy storage plants also use industrial rechargeable batteries for load leveling, where they are used to store electric energy for the peak loading periods. Emerging applications in hybrid electric vehicles/electric vehicles are driving the technology to increase the lifetime of vehicles by reducing the cost and weight. Rechargeable batteries have higher initial cost, but the total cost of use and environmental impact are lower than disposable primary batteries, although they are accounted as pseudopollution contributors because the electricity consumed by them for charging is produced from the combustion of fossils or oil. Normally, new rechargeable batteries have to be charged before their use, but the newer low self-discharge batteries hold their charge for many months and are able to supply charges to up to 70% of their rated capacity. The energy used to charge rechargeable batteries usually comes from a battery charger that uses AC mains electricity, and it will take a few minutes (rapid chargers) to several hours to charge a battery. Since the end of twentieth century, in the United States, Japan, and Europe, the market of rechargeable batteries became vibrant and extremely attractive, as the demand for rechargeable batteries is growing twice faster than that for nonrechargeable

ones. Still there is no *best battery* in the market, but there are a handsome variety of batteries in the market for different situations, likewise, batteries for torpedoes must be stable during storage and must give high power for a short time, whereas batteries for submarine need giant rechargeable ones when submerged.

Unlike batteries, which store energy chemically, capacitors store energy as an electrostatic field. A typical battery is known for storing a lot of energy and little power, whereas a capacitor can provide large amounts of power, but low amounts of energy. A capacitor is made of two conducting plates and an insulator called the *dielectric*, which conducts ionically but not electrically. Few important batteries are described below.

1.6.1

Lead-Acid Batteries

Lead-acid batteries revolutionize the portable power and fall into the classical category invented by French physicist Gaston Planté in 1959 [27]. They consist of six cells of 2 V nominal voltage, and each cell is composed of a lead dioxide cathode, a sponge metallic lead anode, and about 37% w/w sulfuric acid solution as electrolyte. Its main discharge reaction at anode is



And the corresponding discharge reaction at cathode is



The thermodynamic reversible potential for the overall cell reaction is 1.93 V, meaning that less number of cells is used to attain a given potential. The optimum operating temperature for the lead-acid battery is 25 °C. For higher power applications, lead-acid batteries with intermittent loads are generally too big and heavy, suffer from a shorter cycle life, and typical usable power down to only 50% DOD. These batteries become the technology of choice for automotive starting, lighting, and ignition (SLI) applications because they are robust, tolerant to abuse, and of low cost. Lead-acid batteries have a huge market as the starter battery for internal combustion engines. Although they have one of the worst energy to weight ratios (35–40 Wh kg⁻¹) but quite good power to weight and energy to volume ratios, their life seldom exceeds 4 years and can be recharged for 300–400 cycles. In a valve regulated lead-acid (VRLA) batteries, electrolytes avoid spilling out, and the hydrogen and oxygen produced in the cells largely recombine into water. Since the 1950s, chemical additives such as EDTA and Epsom salts [28] have been used to reduce lead sulfate buildup on plates and improve battery condition when added to the electrolyte of a vented lead-acid battery. EDTA can be used to dissolve the sulfate deposits of heavily discharged plates. Residual EDTA in the lead-acid cell forms organic acids that will accelerate corrosion of the lead plates and internal connectors. Epsom salts reduce the internal resistance in a weak or damaged battery and may allow a small amount of extended life. Heavy metal elements used in their

fabrication makes them toxic, and their improper disposal can be hazardous to the environment.

1.6.2

NiMH Batteries

An NiMH battery is similar to the nickel-cadmium cell and was invented in 1967 [29]. The Ni-MH battery uses a hydrogen-absorbing alloy (sintered $Ti_2Ni + TiNi + x$ or the presently used AB_5 , where A is a rare earth mixture of lanthanum, cerium, neodymium, praseodymium and B is nickel, cobalt, manganese, and/or aluminum, and AB_2 compounds, where A is titanium and/or vanadium and B is zirconium or nickel, modified with chromium, cobalt, iron, and/or manganese) as the negative electrode (negative electrode of Ti–Ni alloy hydride phases, US patent US 3,669,745 (13 June 1972), inventor: K. D. Beccu of Battelle, Geneva R&D Center); nickel oxyhydroxide (NiOOH) as the positive electrode developed by Dr Masahiko Oshitani; and usually, 28% potassium hydroxide as the alkaline electrolyte. For separation, hydrophilic polyolefin nonwovens are used. Respective cathodic and anodic reactions of the Ni-MH batteries can be written as follows:

Cathode:



Anode:



Ni-MH batteries can possess 2–3 factors higher capacity (1100–3100 mAh at 1.2 V), the same as an equivalent size nickel-cadmium battery. Its volumetric energy density (140–300 Wh l^{-1}) is similar to that of the lithium ion cell (250–360 Wh l^{-1}), significantly better than that of nickel-cadmium battery at 50–150 Wh l^{-1} , but its self-discharge is higher (30% per month). It can retain specific energy of approximately 30–80 Wh kg^{-1} and a specific power of around 250–1000 W kg^{-1} with a reasonable deep life cycle of 500–1000 cycles (DOD = 100%), and this has led to the new environmentally friendly high-energy NiMH cells [30]. Low internal resistance allows Ni-MH cells to deliver a near-constant voltage until they are almost completely discharged. Modern Ni-MH cells contain catalysts to immediately deal with gases developed as a result of overcharging, without being harmed ($2 H_2 + O_2 + catalyst \rightarrow 2 H_2O + catalyst$). However, this works only with overcharging currents of up to 0.1 C and is used to detect the safe end-of-discharge voltage of the series cells and autoshtutdown. Ni-MH cells are used to power the devices such as digital cameras, GPS receivers and personal digital assistants (PDAs), flashlights, and some toys or video games. Improper disposal of Ni-MH batteries poses less environmental hazard than that of Ni-Cd cells because of the absence of toxic cadmium. Although lithium ion batteries (LIBs) have a higher specific energy than NiMH batteries, they also have a much lower shelf life and are significantly more expensive to produce. Currently, more than 2 million hybrid cars worldwide are running with Ni-MH batteries [31], for

example, Prius, Lexus (Toyota), Civic, Insight (Honda), and Fusion (Ford). Many of these batteries are manufactured by Panasonic (PEVE) and Sanyo.

1.6.3

Li-Ion Batteries

A LIB was first proposed by M. S. Whittingham of Binghamton University, Exxon, in the 1970s using titanium(II) sulfide as the cathode and lithium metal as the anode, and it belongs to the rechargeable type of batteries. The primary functional components of LIBs are anode, cathode, and electrolyte [32]. Lithium ion cell uses an intercalated lithium compound (Li in porous carbon or graphite) as the anodic material instead of metallic lithium. A layered oxide (such as lithium cobalt oxide) or a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide) material is used as cathode. Pure lithium is niche industrial material of very reactive nature. It reacts vigorously with water to form lithium hydroxide and liberate hydrogen gas. Thus, nonaqueous electrolytes are required for LIBs. A typical mixture of nonaqueous organic carbonates such as ethylene carbonate or diethyl carbonate containing the complex of lithium ions (lithium hexafluorophosphate (LiPF_6), lithium hexafluoroarsenate monohydrate (LiAsF_6), lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), or lithium triflate (LiCF_3SO_3)) is used as the electrolyte. Lithium ions that move from the negative electrode to the positive electrode during the discharge process through the nonaqueous electrolyte and separator diaphragm move back when charging.

The cathodic half reaction of LIB is



And another anodic half reaction is



Recently, novel architectures fabricated using nanotechnology have been employed to improve the performance of LIBs. Chemistry, performance, cost, and safety are the characteristics that are basic to the electrode material used. LIBs became technological of today's choice because of the qualities of the best energy to weight ratios (specific energy density, 150–250 Wh kg^{-1} ; volumetric energy density, 250–530 Wh l^{-1} ; specific power density, 300–1500 W kg^{-1}), no memory effect, and a slow loss of charge when not in use. Beyond their popularity for portable electronics, LIBs are also the growing interest in military, electric vehicles, and aerospace applications because of their high energy density. There are few disadvantages of LIBs, that is, its internal resistance is higher than other rechargeables such as Ni-MH and Ni-Cd batteries and increases with both cycling and age thus reducing the cell's ability to deliver current. Charging forms electrolyte deposits that inhibit ion transport; high charging levels with elevated temperatures (whether from charging or ambient air) also hasten their capacity. LIBs with a lithium iron phosphate cathode and graphite anode have a nominal open-circuit voltage of 3.2 V and a typical charging voltage of 3.6 V. LIBs could not be charged fast and needed

at least 45 min to 2 h to fully charge. In 2007, Cui and colleagues at Stanford University's Department of Materials Science and Engineering discovered that using Si/Ge nanowires as the anode of an LIB increases the volumetric charge density of the anode up to a factor of 10 [33, 34].

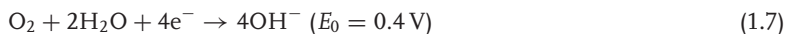
Further advancement in LIB is made by replacing lithium salt electrolyte in an organic solvent with a solid polymer composite such as polyethylene oxide or polyacrylonitrile [35]. The advantages of Li ion polymer over the LIBs include potentially lower manufacturing cost, adaptability to a wide variety of packaging (in various shapes), increased life cycle, slow degradation rate, and ruggedness. Lithium ion polymer batteries started appearing in consumer electronics around 1996 [36]. However, in recent years, manufacturers have been declaring upward of 500–10 000 charge–discharge cycles before the capacity drops to 80%. Li poly batteries are gaining favor of the world in radio-controlled aircraft and radio-controlled cars, airsoft gun, PDAs, and laptop computers, such as Apple's MacBook family, Amazon's Kindle, Lenovo's Thinkpad X300 and Ultrabay Batteries, the OQO series of palmtops, the HP Mini, and Dell products featuring D-Bay batteries, where the advantages of both light weightness and greatly increased run times can be sufficient justification for their price. They can also be found in small digital music devices such as iPods and Zune and other MP3 players, the Apple iPhone, gaming equipment such as Sony's Playstation 3, and wireless controllers.

1.6.4

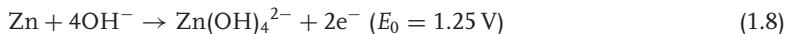
Zinc–Air Batteries

Zinc–air batteries [37] have some properties resembling the fuel cells, such as zinc electrode consumed as fuel, and the reaction rate can be controlled by varying the air flow. Commercial production began in 1932, when George W. Heise and Erwin A. Schumacher of the National Carbon Company (US patent 1899615(A) dated: 28 January 1933) built these cells. Zinc–air battery consists of a porous *air* electrode (cathode) made of carbon that draws in atmospheric oxygen, which gets absorbed into the electrolyte (aqueous KOH) through a gas-permeable and liquid-tight membrane (also acts as catalyst) to the zinc electrode (anode), where oxidation of zinc releases electrons to generate a current with ZnO production.

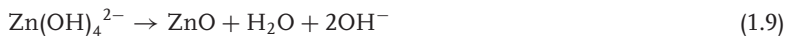
Cathode (porous air-carbon electrode):



Anode (Zn electrode):



Fluid reaction:



Overall reaction:



The cell voltage for the above theoretical chemistry is 1.65 V; however, almost all designs are optimized for <math><1.4</math> or 1.3 V in order to achieve longer lifetimes. Recharging process is the reversal of the above reactions: zinc oxide is converted back to zinc at negative anode and oxygen is released at the positive air electrode. During discharge, Zn is converted to ZnO, which is replaced through mechanical charging in which discharged zinc cartridges are replaced with fresh zinc cartridges. Repeated charge–discharge cycles deactivate (slowing or stopping the oxygen reactions) the air electrode and gradually tend to fill its pores with the liquid electrolyte. The battery can also fail if it dries out or if zinc builds up unevenly, forming branchlike structures that create a short circuit between the electrodes. Like all other battery technology involving Ni-MH, lead-acid, and zebra batteries, zinc–air batteries are safer than LIBs (requires much more extensive electronic monitoring) because they are short-circuit proof, and they do not contain volatile materials, hence, they do not catch fire or explode during a car crash. Zinc–air batteries require filters to remove carbon dioxide from the air for their use; the removal is via passing air through the inexpensive hydroxide scrubbers where it is fixed to carbonate as a support to purify the air. Zinc–air batteries can beat petrol-dependent road transportation for electric propulsion with their unique capability of anthropogenic CO₂ removal. A new breed of rechargeable zinc–air batteries (Figure 1.8, ReVolt, Staefa, Switzerland) will soon to be available in market and may replace LIBs in cell phones, laptops, and other consumer items. LIBs store only one-third of the energy and cost around twice as much as the new breed of rechargeable zinc–air batteries [37]. Ni-MH and LIBs are very expensive (\$500 k Wh⁻¹), whereas the relative cost of zinc–air batteries is only \$60 k Wh⁻¹ but still are a favorite technology for battery industry. The zinc–air systems are quite popular among their category because of the use of nontoxic, inexpensive, and abundantly available raw materials; the high energy density (1480–9780 Wh l⁻¹); the high energy per unit of weight (470 (practical), 1370 (theoretical) Wh kg⁻¹); and an excellent shelf life with a self-discharge rate of only 2% per year when sealed, but they have a low specific power (100 W kg⁻¹). Their few disadvantages are sensitivity to extreme temperature and humid conditions, chemicals tend to dry out, high self-discharge, high internal resistance, and low recycle lifes. In the light of the low cost, material availability, safety, environmental aspects, and financial constraints faced by the world today, governments should prioritize zinc–air batteries to power

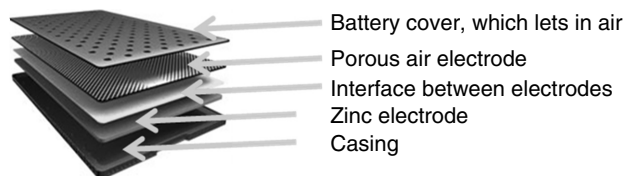


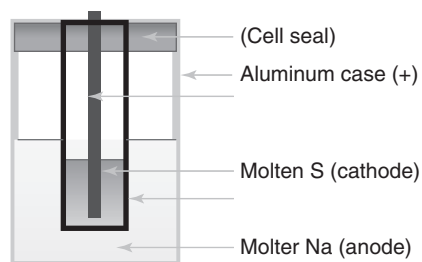
Figure 1.8 Illustration of the multilayered structure of an unpacked ReVolt rechargeable zinc–air battery. (ReVolt, Staefa, Switzerland.)

automobiles [38]. Zinc–air button cells are commonly used for watches and hearing aids. Larger types are employed as prismatic or cylindrical cells for telecoms and railway remote signaling and for safety lamps at road and rail construction sites, as power sources for electric fences, and in film cameras that previously used mercury batteries. Very large batteries are used for electric vehicle propulsion.

1.6.5

Liquid Redox Batteries

Liquid-metal batteries are fabricated by molten anode and cathode materials separated by solid electrolyte (a beta-aluminum oxide ceramic ion conductor). They are of low manufacturing cost, of extremely high power density, and are suitable for grid-scale storage. A classic example of this category is sodium–sulfur batteries (Figure 1.9) [39], discovered in 1980 and consisting of molten sodium anode and molten sulfur cathode, separated by conductive ceramic electrolyte sodium beta-alumina (approximately 11 parts of aluminum oxide Al_2O_3 and 1 part of sodium oxide NaO , with a melting point of 2100°C). Sodium melts at 98°C and sulfur at 113°C , but the operating temperature is around 350°C . During discharge, electrons are stripped off the sodium atoms and flow through the external load to the sulfur cathode. The positively charged sodium ions move through the electrolyte where they react with the sulfur and the electrons to produce sodium polysulfide. During recharge, the applied voltage strips electrons from the sodium polysulfide returning it back to sodium ions. The sodium ions now cross the electrolyte into the sodium where they are reunited with their missing electrons to form sodium atoms. The sodium–sulfur battery can have very high energy ($50\text{--}200\text{ Wh kg}^{-1}$) and power densities ($100\text{--}200\text{ W kg}^{-1}$) and a limited shelf life, typically of the order of 2–5 years. One of the key advantages of batteries with liquid electroactive materials is that there are no morphological changes on cycling that can offer infinite life cycle to the active materials, but the solid electrolyte is susceptible to mechanical degradation by the phase change that occurs as the sodium ions are reduced to the metallic state. In the new self-assembling liquid-metal batteries,



Typical sodium–sulfur battery

Figure 1.9 Schematic representation of the typical sodium–sulfur battery, as liquid redox battery.

molten salt serves as both the separator and electrolyte of molten electrodes. Density differences allow two of the three liquid layers to float on the heaviest layer. The very high ionic conductivity of the electrolyte allows for extreme power density, well suited for grid-scale power storage. The safety issues implicit in molten materials and high operating temperature made them not practically attractive for use in electric vehicles, but this problem may be resolved in time. In the proof-of-concept cell by Donald Sadoway's research group at MIT, the three layers, from bottom to top, antimony, sodium sulfide, and magnesium, are expected to be able to handle 10 times the current of typical batteries used in power plants. During discharge, the top and bottom layers are consumed to form magnesium antimonide, which dissolves in the electrolyte. Upon recharge, the metal layers are reformed. New patent pending liquid batteries are designed by Sadoway and his team, including graduate student David Bradwell, using low-cost and abundant materials. The three materials are chosen so that they have different densities that allow them to separate naturally into three distinct layers, with the salt (Mg_3Sb_2) in the middle separating the two metal layers (Mg (top) and Sb (bottom)) and are operated at about 700°C ; if corrosion issues for the electrodes and container can be resolved, the cycle life of these batteries might be nearly infinite. Because of its high energy density, the Na-S battery has been proposed for power grid [40], transport and heavy machinery, and space applications [41].

1.7

Light Fuel Generation and Storage: Water Electrolysis, Chloro-Alkaline Electrolysis, Photoelectrochemical and Photocatalytic H_2 Generation, and Electroreduction of CO_2

Light fuel hydrogen has attracted great attention from environmentalists, scientists, and industrialists as a benign fuel of future because of its capability to produce pollution-free energy and because it has one of the highest energy density, that is, values per mass of 140 MJ kg^{-1} . The majority of hydrogen used in industries is derived from fossil fuels or cleavage of water. Currently, a majority of industrial hydrogen need is satisfied from conventional sources (coal, oil, and natural gas), which contains about 10% CO_2 with hydrogen gas, and only 4% of H_2 comes from electrolysis, which is the cheapest method to generate hydrogen ($\$3.51$ per kg). Central to the success of hydrogen technology is the efficient generation of hydrogen from renewable sources (such as solar/wind) powered by water cleavage. Water splitting by electrolysis, uses the most expensive proton exchange membrane (PEM) and liquid electrolyte (KOH) or thermochemical process (need a temperature of $700\text{--}1000^\circ\text{C}$). Wind energy, the most cost-effective renewable energy source, is also used to electrolyze water (costs about $\$6.64$ per kg per H_2 if grid back up used). Biomass with solar energy costs $\$7.05$ per kg H_2 production. Solar energy either by electrolysis (PV) or using photoelectrochemical cell now costs $\$2.82$ per kg, but solar energy is available only 20% of the time. Following are the advance techniques to produce and use light fuels (H_2 , CO_2).

1.7.1

Water Electrolysis

In 1789, Jan Rudolph Deiman and Adriaan Paets van Troostwijk produced electricity from water using an electrostatic machine by discharge on gold electrodes in a Leyden jar [42]. In 1800, the *voltaic pile* was invented for the electrolysis of water by Alessandro Volta. Finally, the electrolysis of water became a cheap method of hydrogen generation using the Gramme machine invented by Zénobe Gramme in 1869. A method of industrial synthesis of hydrogen and oxygen through electrolysis of water was developed by Dmitry Lachinov in 1888 [43]. Decomposition of pure water into hydrogen and oxygen at standard temperature and pressure is not favorable in thermodynamic terms. Water electrolysis does not convert 100% of the electrical energy into the chemical energy of hydrogen. For a well-designed cell (Figure 1.10), the largest overpotential required for the four-electron oxidation of water to oxygen at the anode. An effective and cheap electrocatalyst to facilitate this reaction has not yet been developed. Platinum alloys are the default state of the art for this oxidation. The simpler two-electron reaction to produce hydrogen at the cathode can be electrocatalyzed with almost no reaction overpotential by platinum or hydrogenase enzyme. In 2008, Kanan *et al.* [44] announced a potentially efficient electrocatalyst (anode) for artificial photosynthesis, composed of a $\text{Co}^{3+}/\text{Co}^{2+}$ metal and phosphate electrolyte. Other researchers are pursuing carbon-based catalysts for the same. Efficiency of converting electrical energy into hydrogen's chemical energy of water electrolysis varies optimally between 50 and 80% [45].

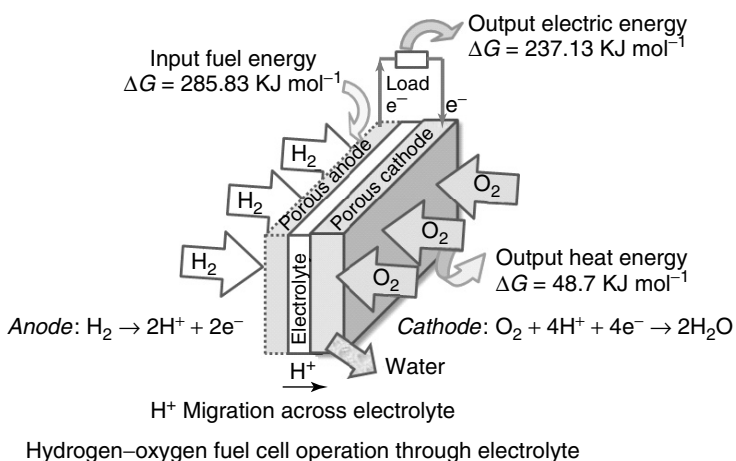


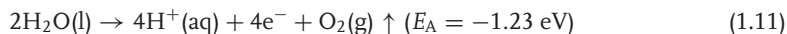
Figure 1.10 Water electrolysis illustrated in hydrogen–oxygen fuel cell with chemical and energetic electrode operations using electrolyte.

1.7.2

Electrochemistry of Water Splitting

Pure water is considerably a bad conductor of current, $0.055 \mu\text{S} \cdot \text{cm}^{-1}$ (one millionth of that of seawater) because it has a low autoionization coefficient, $K_w = 10 \times 10^{-14}$ at room temperature that leads electrolysis of pure water very slowly or not at all. Thus electrolysis of pure water requires excess energy in the form of overpotential to overcome various activation barriers, which enhance the rate of water autoionization. In a properly designed water-electrolysis cell, two electrodes (anode and cathode) are placed in the water and connected by external electrical power source. Hydrogen appeared at the cathode (the negatively charged electrode, where electrons reduce the water), and oxygen appeared at the anode (the positively charged electrode, where oxidation takes place) in 2 : 1 ratio. The efficacy of electrolysis is increased by the addition of an electrolyte (such as solid polymer membrane, Nafion; strong acids, H_2SO_4 ; or a strong base, NaOH , KOH) and electrocatalysts. A solid polymer electrolyte can also be used, such as Nafion, and when applied with a special catalyst on each side of the membrane can efficiently split the water molecule with as little as 1.8 V power supply.

Anode reaction:



Cathode reaction:



Thus, the standard potential of the water-electrolysis cell is -1.23 V at 25°C at $\text{pH } 0$ ($\text{H}^+ = 1.0 \text{ M}$). It retains -1.23 V at 25°C even for $\text{pH } 7$ ($\text{H}^+ = 1.0 \times 10^{-7} \text{ M}$) based on the Nernst equation. This endothermic reaction involves a change in Gibbs free energy $\Delta G = +2.46 \text{ eV}$ or $237.2 \text{ kJ mol}^{-1}$. The negative voltage indicates that the Gibbs free energy for electrolysis of water is greater than zero. The system must be provided with sufficient energy for the dissociation of water plus the energy to expand the produced gases.

1.7.3

Chlor-Alkaline Electrolysis

Chlorine, one of the most important bulk chemicals in the world, is produced by the electrolysis of brine (highly conducting sea water) [46]. Chlorine is used in the day-to-day life as water purifier and is also an essential part in the chemical building block, resulting in a myriad of reactions and products in the major plastic, pharmaceutical, inorganic, and fine chemical and specialty industries [45]. In chlor-alkali electrolysis (Figure 1.11), an air-oxygen gas-diffusion electrode or traditional hydrogen-evolving electrode is used as a cathode, a nickel wire mesh as a counter electrode in 8 M NaOH , and Hg/HgO as reference electrode. Coating of polytetrafluoroethylene (PTFE) suspension was performed on gas-diffusion electrode, shielded by an active layer made up of catalysts [46, 47] containing the

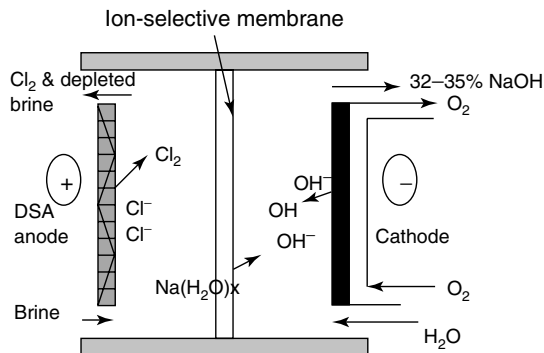


Figure 1.11 Graphical illustration of chlor-alkaline cell.

mixture of perovskite ($\text{La}_{0.1}\text{Ca}_{0.9}\text{MnO}_3$) and the pyrolysis product of cobalt tetramethoxyphenylporphyrin (CoTMPP) with less proofed carbon. In the electrolytic process, during the following overall reaction for every ton of chlorine produced, about 1.1 tons of caustic is generated and 28 kg hydrogen is evolved as a by-product. Four percent of total worldwide hydrogen production is created by electrolysis. The majority of this hydrogen is produced by chlor-alkali electrolysis, where, the chloride ions are oxidized to chlorine and water is reduced to hydrogen as shown in the following reaction.

Overall reaction:



It is an energy intensive process, with an electrical power consumption between 2100 and 3300 kWh per unit time. The amount of Cl_2 generation depends on the operating parameters and the type of the process. There are three major processes based on mercury, diaphragm, and membrane cells in use for the electrolysis. In the year 2001, the total world production of chlorine was about 43.3 million tons, and 18% of this production was met by the mercury cell technology, whereas the remaining 82% included diaphragm (49%) and membrane cell (28%) technologies, and others (5%). Hofmann voltametric, high-pressure (120–200 bar), high-temperature electrolyses used for chlor-alkaline electrolysis are also in practice [48, 49].

1.7.4

Photoelectrochemical and Photocatalytic H_2 Generation

Global energy needs for sustainable development demands 50% increase by 2030. The alternative energy source *the sun* is able to obtain the target by using solar energy to split water into hydrogen and oxygen as a cost-effective storage of solar energy in chemical energy for its large-scale utilization. Nature provides us a blueprint of water-splitting reaction in the form of photosynthesis for storing

sunlight in form of chemical energy. Laboratory-designed artificial photosynthesis required photocatalyst, water, and sunlight to split the water into hydrogen and oxygen in 2:1 ratio. A range of metal oxides, sulfide, nitrides, (oxy)sulfides, and (oxy)nitrides containing either transition metal cations with d^0 electronic configuration (e.g., Ti^{4+} , Nb^{5+} , and Ta^{5+}) or typical cations with d^{10} electronic configuration (e.g., Ga^{4+} , Ge^{4+} , and Sn^{4+}) as principal cation components have been reported as active photocatalysts for overall water splitting. Photocatalytic reaction involves three basic steps: (i) the photocatalyst absorbs more photon energy (sunlight) than the band gap energy of the material and generates photoexcited electron-hole pairs in the material bulk; (ii) the photoexcited charges separate and migrate to the different sites of the photocatalyst's surface without recombination; and (iii) water is reduced and oxidized by the photogenerated electrons and holes to produce H_2 and O_2 , respectively. The first two steps are strongly dependent on the structural and electronic properties of the photocatalyst, whereas the third step is promoted by the presence of a solid cocatalyst (Figure 1.12). The cocatalyst is typically a noble metal or metal oxide or a combination of both, loaded onto the surface of photocatalyst as a dispersion of nanoparticles to produce active sites and reduce the activation energy for gas evolution. To date, various transition metal oxides, including NiO_x , RuO_2 , RhO_x , IrO_2 , and $RhCr_2O_3$, have been applied as a cocatalyst for photocatalytic overall water splitting. Despite a plentiful library of photocatalytic materials mostly active in UV light (5% of sunlight spectrum), visible light-driven photocatalyst with high efficiency is still one of the *holy grails* of material chemistry. Few photocatalysts reported with remarkable efficiency are $(AgIn)_xZn_{2(1-x)}S_2$ [50], $ZnS-CuInS_2-AgInS_2$ [51], La-doped $NaTaO_3$ [52], Ni-doped $InTaO_4$ modified with RuO_2 or NiO as the cocatalyst [53], $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ [54], $SrTiO_3$, BaO-doped

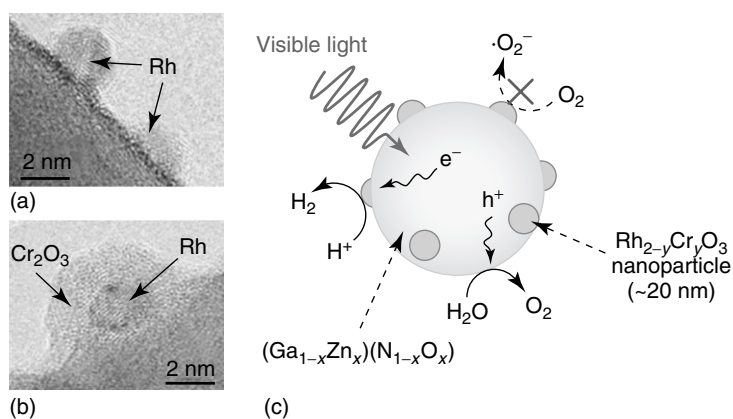


Figure 1.12 Loading of cocatalyst on the surface of the basic photocatalyst and its role in controlling recombination reaction of electrons and protons. HR-TEM images of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ ($x = 0.12$) with

photodeposited Rh (a) before and (b) after further photodeposition of a Cr_2O_3 shell. (c) Schematic view of photocatalytic oxidation and reduction sites [54]. (Copyright American Chemical Society Publications.)

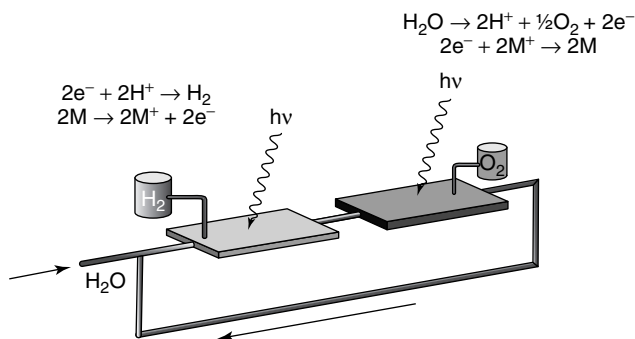


Figure 1.13 Schematic of a dual-bed photocatalytic water-splitting system [60].

$La_2Ti_2O_7$ [55], and $K_3Ta_3B_2O_{12}$ [56]. Photoelectrochemical water-splitting technology is economically superior to electrolysis of water for electricity production because of the single-plant massive photoproduction of clean hydrogen fuel. Titania (TiO_2) was the first material described as a photoelectrochemical water-splitting catalyst, but because of its wide band gap, 3.2 eV, it is able to work in UV light. Fujishima and Honda, in 1972, described an electrochemical cell consisting of an n-type TiO_2 (rutile) anode and a Pt black cathode for photoelectrochemical water splitting. Much attention has been given to photoelectrocatalytic splitting of water using metal oxide or nitride semiconductors, for example, ZnO, GaN, TiO_2 , WO_3 , and Fe_2O_3 , to supply clean and recyclable hydrogen energy. Advancements such as introduction of nanostructures; elemental doping with N, C, P, S, and dyes (Ru complexes); and quantum dot (CdS, CdSe, InP, CdTe, Bi_2S_3) sensitization of based material are also in practice. Bockris and Reddy [57] made their effort to produce faceted TiO_2 (about 1000-fold increase in surface area) and decorated it with dye with a suitable photoreceptor (bipyridyl complexes of ruthenium), then they became capable of harvesting visible light. Key point is the use of traces of electrocatalyst added to the surface of both photoanode and photocathode [58, 59] to an appropriate extent. Use of a perylene diimide derivative as the O_2 -evolving photocatalyst and copper phthalocyanine as the H_2 -evolving photocatalyst in the IO_3^-/I^- redox electrolyte demonstrates the feasibility of continuous closed-cycle dual-bed photocatalytic water splitting (Figure 1.13) [60]. Recently, artificial inorganic leaves have been developed as biotemplates [61] by using catalysis modules (Pt/N- TiO_2) for enhanced light-harvesting, and photocatalytic water-splitting activities stem from the reproduction of the leaves complex structures and self-doping of nitrogen during synthesis (Figure 1.14).

1.7.5

Carbon Dioxide Reduction

Before the industrial revolution, CO_2 concentration in the atmosphere was about 290 ppm. By 1995, it had reached 360 ppm. Today, it is about 410 ppm, and

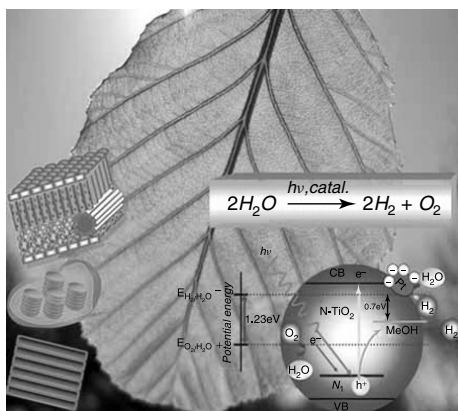


Figure 1.14 Artificial inorganic leaves for efficient photochemical hydrogen production inspired by natural photosynthesis [61].

extrapolation of the present data raised it up to 560 ppm in 2060, accompanied with rise in temperature to about 1.5 K at the equator and a corresponding estimated increase in the sea level by 50 cm and 3.2 K temperature at poles will reduce the reflectivity of the region (water is dark and ice is bright) eventually increasing the earth's average temperature [62]. The situation is becoming more and more critical day by day. One way to deal practically with this problem is to fix this undesirable CO₂ into hydrogen carrier liquid, that is, methanol, to be used in fuel cells [63]. Fisher and Prziza [64] were first to observe the 100% electrochemical reduction of CO₂ to HCOOH. Photoelectrochemical conversion of CO₂ to oxalic acid was performed using InP-electrode (cathode) in two-photon cell having LaCrO₃-TiO₂ as photoanode [65]. An 18-crown-6-ethers-decorated-CdTe electrode in the presence of tetraalkylammonium ions reduces CO₂ mainly to CO with a small amount of CH₃OH [66]. A major breakthrough would be the discovery of a suitable effective catalyst or photocatalyst in CO₂ fixation for the reduction of the major greenhouse gas CO₂ into a useful chemical, that is, methanol (MeOH), using H₂ gas supply.



Inspired by photosynthetic reactions in plants, now a reasonable goal of electrochemical science is to fix planetary CO₂ by photochemical/photoelectrochemical reaction to form MeOH, and the further goal would be based on the production of synthetic food and textile from water, solar light, atmospheric CO₂, and nitrogen (bacteria). However, it is also possible to use CO₂ in electrochemical synthesis of organic compounds that exemplify in the formation of phenyl acetic acid by benzyl chloride [67].

1.8

Fuel Cells: Fundamentals to Systems (Phosphoric Acid Fuel Cells, PEM Fuel Cells, Direct Methanol Fuel Cells, Molten Carbon Fuel Cells, and Solid Oxide Fuel Cells)

Fuel cells are compact electrical energy producer devices that consume fuels (chemical energy) via fuel (e.g., hydrogen, methanol, and hydrocarbon) oxidation at anode and reduce oxygen (usually comes from air and triggered into solution) as oxidant at counter cathode on immersing into electrolyte. The electrolyte is specifically designed so that ions can pass through it, but the electrons cannot. The free electrons travel through a wire, creating the electrical current. The revolutionary advantage of fuel cells over other energy-producing devices is that the free highly dense energy directly comes out as pollution-free electrical energy without planetary warming. As no combustion reactions are involved in fuel cells, they do not produce any of the undesirable products (CO_2 , SO_2 , oxides of nitrogen, or particulate matters), which are normally associated with the oxidation of fossil fuels in conventional energy conversion systems. Thus, fuel cells are environmentally friendly. However, fuel cells offer the additional advantages of lighter weight, noiselessness, nonpolluting, and vibration-free operation than batteries that require recharging after use. For these reasons, they are beloved candidates to be used as battery's supplements. Formal discovery of fuel cell principle is attributed to Sir William Grove (February 1839) [68] as he passed current through the connecting wire between anode that was bubbled with hydrogen and its counter electrode was blown with oxygen from air, the device was named as *gas voltaic battery* [2] (Figure 1.15). Francis Thomas Bacon made pioneer contribution in the development of fuel cells in 1959. NASA uses Bacon's cells for auxiliary power in space vehicles, as they are three times as effective as any other method of providing energy on board. Fuel cells have the potential to replace the internal combustion engine in vehicles and to provide power in stationary and portable power applications because they are energy efficient, clean, and fuel flexible. Direct fuel cells can feed hydrocarbons directly to the fuel cell stack, without requiring an external *reformer* to generate hydrogen [69]. Fuel cells are thermodynamically open systems that work spontaneously and go down the free energy gradient by

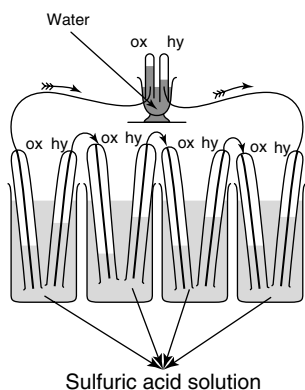


Figure 1.15 Sketch of the first hydrogen–oxygen Grove's fuel cell invented in 1839. The dark lines in the central of the tubes are platinumized-foil electrodes [68b].

consuming reactant from an external source, which must be replenished. There are two governing factors in fuel cells. First, is the exchange current density of cathode that causes low overpotential (higher limiting current density $i_0 \sim 10^{-3} \text{ A cm}^{-2}$), resulting in high efficiency of chemical energy conversion. Second, is the limiting current density of cell that depends on the type of electrode. Flat-type electrodes show maximum power density, $<1 \text{ mW cm}^{-2}$; on the other hand, porous electrodes make the limiting current 100–1000 times greater, with power densities of up to 1 W cm^{-2} . Fuel cells are categorized on the basis of the electrolyte employed and their operating temperature range, that is, low-temperature fuel cells (alkaline, proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC)) and high-temperature fuel cells (phosphoric acid fuel cell (PAFC), molten salt, and solid oxide fuel cells). Low-temperature fuel cells use a platinum catalyst. Therefore, these fuel cells are prone to catalyst poisoning by impurities. Although, there are sufficient platinum resources for the future, soaring prices of precious platinum has led recent research to replace platinum with a material that may be less susceptible to poisoning, economic by cost, safe from an environmental point of view with improved lifetime. Considerably, gold and palladium coated [70] iron and sulfur instead of pure platinum through an intermediate conversion by bacteria would lower the cost of a fuel cell substantially from \$1500 to \$1.50.

1.8.1

Alkaline Fuel Cells

Alkaline fuel cells (AFCs) are economically qualified for providing a power of 10–100 kW, can work optimally at 80°C with a cell efficiency of 60–70%, and use basic solutions as electrolytes, hence, a wide range of electrode catalysts (relatively inexpensive materials) are available for them, whereas the cells using acid solution or high temperature can use only a noble metal as electrode material. At the time of being switched on, they can produce almost one-fourth of the power that is produced at optimal temperature, whereas intermediate- and high-temperature cells need auxiliary power source to start them and warm them up. However, AFCs have a disadvantage: air contains CO_2 with O_2 and forms carbonates in alkaline solution and blocks the pores of porous electrodes, thus CO_2 -free air is used in cells. Bacon cells used in Apollo moon project are AFCs run on pure H_2 and O_2 .

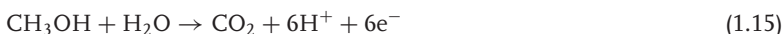
1.8.2

Direct Methanol Fuel Cells

DMFCs are qualified for providing a power of 100 mW to 1 kW and 20–30% efficiency and can produce a small amount of power over a long period. Low-volume, lightweight packaging, zero-emission power system, low operating temperature ($50\text{--}120^\circ\text{C}$), and no requirement for a fuel reformer unit made the DMFCs an excellent candidate for very small to mid-sized applications [71]. DMFC systems are used to power portable applications (smaller vehicles such as forklifts and tuggers, small portable power supply units for household use, cell phones, digital

camera, laptop, music systems, soldier-carried tactical equipment, battery chargers, and autonomous power for test and training instrumentation) and also as auxiliary power units (APUs) for some niche transport sectors such as marine and submarine vehicles, scooters, and motorbikes [72, 73]. Surya Prakash and Nobel laureate George A. Olah invented the present breed of fuel cells that would directly convert methanol to electricity using a Nafion membrane and platinum electrodes for both half-reactions, in 1992 [74]. DMFC is similar to the PEMFCs in that the electrolyte is a polymer and the charge carrier is the hydrogen ion (proton). However, the liquid methanol (CH_3OH) is oxidized in the presence of water at the anode, generating CO_2 , hydrogen ions, and electrons that travel through the external circuit as the electric output of the fuel cell. The hydrogen ions travel through the electrolyte and react with oxygen from the air and the electrons from the external circuit to form water at the cathode, thus completing the circuit.

Anode reaction:



Cathode reaction:



Overall cell reaction:



Low concentration of methanol (1–3 M) is preferred in DMFCs because methanol has the tendency to diffuse in high concentrations through the membrane to the cathode, without reacting with anode (methanol cross over), where its concentration becomes zero because of the rapid consumption by oxygen. It limits the maximum attainable current and loses almost half of the methanol. Oxidization of methanol at cathode contributes to the loss of cell voltage potential and produces carbon monoxide that strongly adsorbs onto the platinum catalyst and reduces the active surface area, thus reducing the performance of the cell. Addition of ruthenium or gold to the catalyst tends to ameliorate this problem because according to the most well-established theory in the field, these catalysts oxidize water to yield OH^\bullet radicals: $\text{H}_2\text{O} \rightarrow \text{OH}^\bullet + \text{H}^+ + \text{e}^-$. These OH^\bullet species oxidizes CO to CO_2 : $\text{CO} + \text{OH}^\bullet \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^-$. Carbon supported Pt-Cr electroanodes also applied to enhance the activity of DMFCs [75]. Low operating temperatures requiring a high noble metal loading to enhance the kinetics of the methanol electro-oxidation reaction and low efficiency and toxic nature of methanol are the prominent factors that often go against its progress.

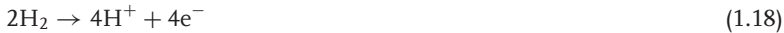
1.8.3

Phosphoric Acid Fuel Cells (PAFCs)

Molten phosphoric acid (H_3PO_4) fuel cells are able to produce <100 MW power at a working temperature of 150–220 °C with a cell efficiency of 80% and cost

at \$4–4.5 per W. Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), a polymer of phosphoric acid usually synthesized at $<150^\circ\text{C}$, is used as the electrolyte in PAFCs and forms ionic solution of considerably high conductivity than the parent acid. The charge carrier in this type of fuel cell is the hydrogen ion (H^+ , proton). This is similar to the PEMFCs where the hydrogen introduced at the anode is split into protons and electrons. The protons migrate through the electrolyte to cathode and combine with the oxygen (which usually comes from air) to produce water. And electrons are routed through an external circuit to cathode where they can perform useful work. This set of reactions in the fuel cell produces electricity and the by-product heat as written below.

Anode reaction:



Cathode reaction:



Overall cell reaction:



In addition, CO_2 in air does not affect the electrolyte or cell performance. Therefore, it can easily be operated with fossil fuel reformer. Simple construction, low electrolyte volatility, and long-term stability are additional advantages associated with PAFCs. But high concentration of H_3PO_4 creates freezing problem when the cell is turned off, requiring auxiliary heating to maintain a temperature of $>40^\circ\text{C}$. Alloys of Pt with Ti, Cr, V, and so on, of small particle size [76] and non-noble metal (hence cheap) electrocatalyst were preferred in PAFCs to achieve high performance in hot acidic solution [77]. Graphite from porphyrine ash applied to keep the central atom apart by preventing the aggregation of particles gives better catalysis [78]. PAFCs are increasingly used in big buildings for light and heat supply that utilize 80% of overall energy instead of 40% of others. Some international brands, which bring PAFCs into limelight, are Plug Power (the United States), International Fuel Cells Corporation (the United States), and Japan's Fuji Electric Corporation, Toshiba Corporation, and Mitsubishi Electric Corporation.

1.8.4

Proton Exchange Membrane Fuel Cells

In the archetypal PEMFC design, a proton-conducting, thin, permeable polymer membrane (the electrolyte) separates the anode and cathode sides and was called a solid polymer electrolyte fuel cell (SPEFC) in the early 1970s till the proton exchange mechanism was well understood. In a typical membrane electrode assembly (MEA), the bipolar electrode plates are usually made of noble metals, nickel, or carbon nanotubes and coated with a catalyst (such as platinum, nano iron powders, or palladium) for higher efficiency [79]. Carbon papers are used to separate them from the electrolyte. PEMFCs possess a cell efficiency of about

40–70%, are qualified for providing 100–500 kW power with suitable operating temperature of 50–120 °C (Nafion) and 120–220 °C (polybenzimidazole (PBI)), and are cost worthy for \$30–35 per W. Ethanol, butanol, hydrogen, and methanol presently made from either natural gas or biomass are utilized as fuel. PEM units are still considered to be the most prevalent alternative because of its operating on stored hydrogen gas. The first major breakthrough for PEM systems came as part of NASA's space program, Project Gemini. Compact design, light-weighted unit with rapid start up, and the use of solid electrolyte rather than a liquid makes the sealing of the anode and cathode gases far easier and cheaper unit to manufacture and can lead to a longer cell and stack life as it is less prone to corrosion than some other electrolyte materials. However, major disadvantages associated with PEM are low operation temperatures, that is, 80 °C, which are not high enough to perform useful cogeneration. Furthermore, in order to achieve the most effective operation of the electrolyte, it must be saturated with water, otherwise the membrane would be cracked causing the breakdown of the cell. Therefore, control of the moisture at the anode and cathode streams becomes an important consideration. The future of PEMFC systems is certainly developing as a promising technology to be utilized in several key market sectors such as cars, buildings, and smaller stationary applications, which span growth opportunities over the short-, medium-, and long-term time frame. Commercially viable PEMFC vehicles are the need to lower the platinum loading of the MEA without loss of performance and to improve the stability of the catalyst with respect to platinum dissolution and carbon-support corrosion [80].

1.8.5

High-Temperature Molten Carbonate Fuel Cells

Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells, which operate at the temperatures of 600 °C or above and are composed of a molten carbonate salt (potassium carbonate, K_2CO_3) mixture as electrolyte, suspended in a porous and chemically inert ceramic matrix of beta-alumina solid electrolyte (BASE) that transports carbonate ions rather than protons (Figure 1.16). The operating temperature of 600–650 °C is lower than that of solid oxide fuel cells (SOFCs) and could be worked up to 50–60% efficiency with an operating power of 100 MW [81]. On utilization of waste heat, overall fuel efficiencies can become as high as 85%. Improved efficiency of MCFCs over PAFCs is a considerable cause for significant reduction in cost. Unlike alkaline, phosphoric acid, and polymer electrolyte membrane fuel cells, MCFCs do not require an external reformer to convert more energy-dense fuels to hydrogen because MCFCs operate at high temperatures that convert these fuels into hydrogen within the fuel cell itself by a process called *internal reforming*, which also reduces cost. MCFCs are not prone to carbon monoxide or carbon dioxide poisoning because the oxidation reactions that occur at anode at high temperature produce steam that was utilized by CO/CO_2 in reforming hydrocarbon fuel inside the anode [82]. Furthermore, they can even use carbon oxides as fuel, making them more attractive for fueling with gases

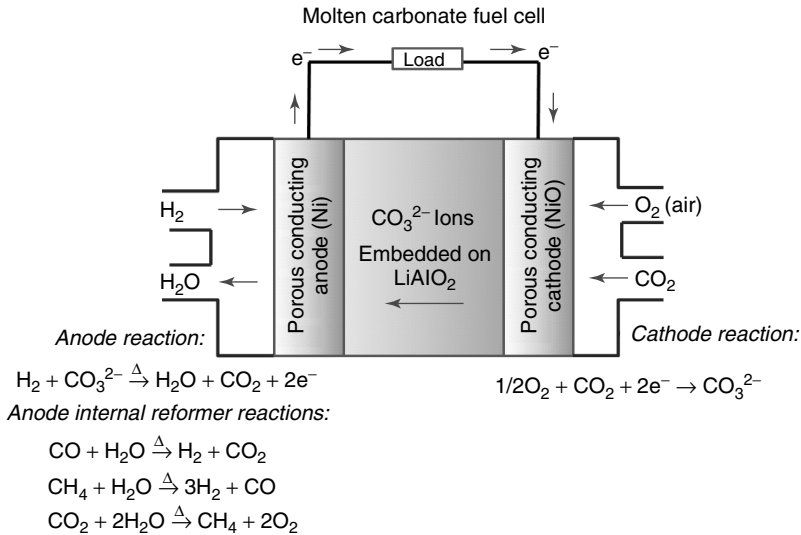


Figure 1.16 Conceptual diagrammatic presentation of the molten carbonate fuel cell, which includes anodic and cathodic chemical reactions with anode internal reformer reactions.

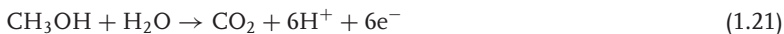
made from coal, and they are highly resistive toward impurities than other fuel cells. Primary disadvantage of current MCFC technology is low durability because the high operating temperatures and corrosive nature of electrolyte accelerate component breakdown that decreases cell life. Scientists are currently exploring corrosion-resistant materials for components as well as fuel cell designs that increase cell life without decreasing performance.

1.8.6

Solid Oxide Fuel Cells

SOFCS were first systematically described by Grubb in 1957. SOFCs work at high temperatures, and ionic conductor or aqueous liquid electrolytes are replaced with well-humidified thin membranes (0.1 mm thick) of perfluorosulfonic acid polymer (Nafion), yttria (Y_2O_3)-stabilized zirconia (ZrO_2), and other such materials between anode and cathode, which can transport protons and oxygen ions, respectively. Their electrode reactions are as follows:

Anode reaction:



Internal reformer reaction:



Cathode reaction:



Overall reaction:



Standard operating temperature of SOFCs is $>250^\circ\text{C}$. SOFCs are extremely advantageous because of the possibility of using a wide variety of fuels [83] such as hydrogen, butane, methanol, and other petroleum products. Nickel and nickel oxide are used as catalyst instead of the costlier platinum, and they also do not experience catalyst poisoning by carbon monoxide, so they do not require high-purity hydrogen fuel. High temperature decreases i_0 in $\eta = RT/F \ln i_0/i$ reduces the overpotential [62] required for given current densities. High-performance cathodes obtained high power density of SOFCs. For larger stationary applications at the level of 10–100 MW, SOFCs offer the additional advantage over conventional power plants of cogeneration of both electric power and low-grade heating. A major disadvantage of the SOFCs is that as a result of the high operating temperature, a considerable constraint on the choice of the electrode materials and unwanted reactions may occur inside the fuel cell [84]. It is very common for SOFCs to build up carbon dust or graphite on the anode, preventing the fuel from reaching the catalyst. SOFCs with nonfluorine membrane (polystyrenesulfonic acid) was used in the Gemini spacecraft. High-temperature cells are envisaged largely for stationary power plants and electrochemical engines in cars.

1.9 Summary

Global energy-need-projections (based on sound scientific facts) for sustainable development suggest a 50% increase in world energy requirement by 2030. Energy demand accompanied by downfall in conventional energy sources, which is associated with a myriad of environmental issues and their very impact on life, grew a worldwide consensus on clean energy that became the highly witted driving force behind the current trends of transition from conventional to renewable energy resources, that is, hydro, biomass, wind, solar, geothermal, and biofuels. In the foreseeable future, the prospect of using renewables made the strong commitments to expand them as alternate energy sources because of their abundance and vast potential that decrease the cost and hold a strong promise to revolutionize the present energy technology to meet future energy demands. After getting the crystal clear picture of past, present, and future energy scenario, we focus on electrochemical technologies for energy storage and conversion devices. This essay reviews the current energy status and applications of advanced technologies for energy generation and concludes with a discussion of the prospects of a future global-scale energy storage and conversion systems based on electrolysis, PV and

photocatalytic hydrogen generation, rechargeable batteries, supercapacitors, and fuel cells. Fundamental issues of electrochemical technologies were scaled-up here with their related safety problems, which have been well understood, and their relevant solutions were short listed, which attracted the world's focus toward sustainable green energy sources.

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