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Nanotechnology in Electrocatalysis for Energy

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Nanotechnology in Electrocatalysis for Energy

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Preface

This book focuses on nanotechnology in electrocatalysis for energy applications. In particular it covers nanostructured electrocatalysts for low temperature fuel cells, low temperature electrolyzers, and electrochemical valorization of carbon dioxide.

In recent years a variety of papers have been published on this subject. Nevertheless, the availability of introductory monographs on such a hot topic is still limited.

Researchers and professionals new to this field often find it difficult to navigate through the huge amount of information being constantly produced in such a quickly growing area. For this reason we have tried to design a book whose function is to provide an introduction to the basic principles of electrocatalysis, together with a review of the main classes of materials and electrode architectures. We feel that this approach has the potential to illustrate the basic ideas behind material design, providing also an introductory sketch of the current research focuses. The book is conceived to be as self-contained as possible. Here and there, especially in the chapters concerning basic thermodynamic and kinetic principles, we advise the reader to refer to the many excellent textbooks that already cover these areas. We hope we have succeeded in making this book readable enough to allow a graduate in technical and scientific disciplines with a fair background in chemistry (i.e. physicists, engineers, chemists, electrochemists, etc.) to understand the basic concepts. A reader with such a background will experience a gentle introduction allowing him to grasp the main design criteria driving the development of new nanomaterials for electrocatalysis. We also hope that the material presented in the book will help the reader to seek more specialized literature, developing his or her own opinion about the pros and cons of the very many existing approaches (at times, a nontrivial task).

The subject has been limited to low temperature electrocatalysis (below 120 °C). We are conscious that this is a limit. But on the other hand, extension to high temperature systems would have required much more space and the illustration of a variety of complex principles, something we believe does not match the original objectives we had for this book.

Discussion focuses on the three main fields where nanostructured and molecular electrocatalysts play a major role: (i) polymer electrolyte membrane fuel cells, (ii) electrolytic hydrogen production, and (iii) CO_2 electroreduction.

The book consists of three parts. After a short introduction (Chap. 1) that reports the general framework and outlines the concept of the book. Part I, entitled *Fundamentals,* then begins. This is aimed at giving an introduction to the basic concepts of electrocatalysis (Chap. 2), also describing the main devices where nanomaterials are exploited (Chap. 3). The text has been organized in such a way that no complex derivations or lengthy descriptions are given. Only the major formulas and concepts are reported in a simple fashion, to help the reader to understand the philosophy behind electrocatalytic material development. This part closes with a discussion of the factors affecting the design of electrocatalysts (Chap. 4), describing the main issues and also stressing the constraints which have to be necessarily accounted for. After such a discussion the role of nanotechnology in addressing the targets for effective electrocatalyst development is considered.

Building upon sound foundations, the description of the various materials begins. Each chapter regarding materials begins with a key concepts paragraph, giving the essential background that lies behind the development of research in each area.

Part II, entitled *Support Materials*, is devoted to catalyst support materials. The part starts (Chap. 5) with a discussion of carbon blacks, the ubiquitous porous carbons widespread in commercial electrocatalyst technology. Then carbon nanomaterials are reviewed, with a special emphasis on the "rising stars," such as carbon nanotubes and graphene. Chapter 6 deals with other support materials. Titania nanotubes and other conducting oxides are considered. These are especially important for fuel cells fed with liquid fuels. The use as innocent support and promoter of the kinetics of a variety of other nanomaterials is also described, completing the scenario.

Part III is entitled *Active Materials*. Chapter 7 describes the main approaches to metal nanoparticle synthesis and the main commercial electrocatalysts. A variety of nanostructured metals with shape and structure control (Chap. 8) are considered. A special emphasis is laid on control of the surface structure, with a discussion of the recent discovery of new synthetic routes to high index faceting for activity enhancement. Chapter 9 reports classes of nanoparticles engineered for the reduction of noble metal loading. The focus is on "hollow" and "core" shell nanoparticles. Chapter 10 reports a "molecular" approach to electrocatalysis. The use of macrocycles and heat treated macrocycles in electrocatalysis is extensively reviewed with a special emphasis on the most recent findings. The description of the breakthrough discovery of organometallic complexes employed in electrocatalysis is also given. The objective is to provide examples of single site processes leading to a completely new approach which could be considered to go "beyond nanotechnology." A short conclusion summarizing the main aspects of each single material category is then reported in Chap. 11.

Acknowledgments

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Part II Support Materials

Part III Active Materials

Part I
Fundamentals

Chapter 1
Introduction

1.1 Key Concepts

The present chapter is intended as a somewhat "non-technical" introduction to the field covered in the book. We have structured it in such a way that the reader may find a short overview of the fundamental issues for which nanotechnology is relied upon to provide solutions. It starts with a short review of the current world energy and resources situation. This is important because the finiteness of resources is not only the reason why we look to renewable energy sources, but it also defines an important constraint to material design. Indeed many of the best known metals which can be used as electrocatalysts in electrochemical energy conversion devices are rare and expensive. For this reason they should be preserved or recycled and used only in negligible amounts in order for these devices to help to obtain a "sustainable" future. Part 2 focuses on environmental issues, stressing the need for a transition to a completely renewable energy system that does not poison our planet. The concept of renewable resources is also defined and some of the most relevant renewable energy resources are reviewed, with a special emphasis on the connection between their application in energy harvesting and electrochemical energy conversion technologies. The concepts of EROEI and net energy are also quickly discussed, together with the approach of Life Cycle Analysis. This is especially relevant for the book, as we believe that both researchers and professionals operating in the field should be aware that the materials they develop are just a small part of a complex system. The purpose of this system is to deliver energy in a clean and efficient way. It is never unworthy to stress that efficiency has to be provided at the level of the whole system. Basically the point is that not only is the performance important, but also the energetic and environmental impact of the materials and the processes used to obtain them. All of which must be carefully considered.

Next we introduce the concept of the hydrogen economy and the use of energy vectors as a part of a sustainable energy paradigm. A short introduction to fuel cells and electrolyzers follows, thus defining the devices where the materials focused on in this book will be potentially exploited. Next we introduce the

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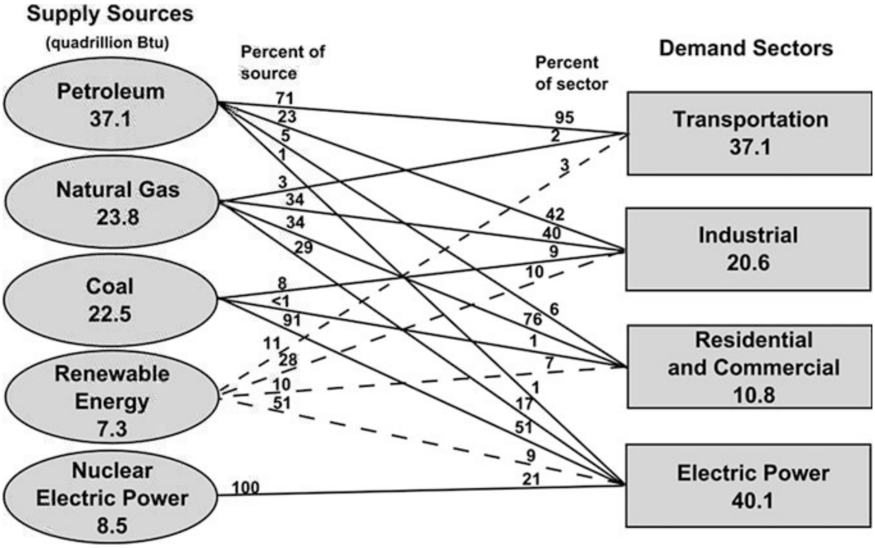
electroreduction of CO_2. This field is much less developed than fuel cells and electrolysis and no commercial devices are at present available. Nevertheless, the valorization of CO_2 is an area of outstanding importance and promises to be one where nanotechnology may give a truly relevant contribution. We will limit our discussion to low temperature devices. A wider discussion is beyond the scope of the book. The need for nanotechnology in energy-related electrocatalysis is then discussed at the end of the chapter where a short presentation of the concept of the book is also given.

1.2 Energy and Resources

The world over the last couple of centuries has experienced an unprecedented global economic development. This has undoubtedly been attributed to the rising availability of fossil energy resources, such as oil, coal, and natural gas. Among these resources the most notable has definitely been oil, as its transformation into liquid fuel provided an impressive energy vector, easily stored and transported and with a large energy density.

Nowadays, almost every aspect of human life, at least in most developed countries, strongly depends on the availability of a large amount of energy and ultimately fossil fuels (Scheme 1.1). The role of fossil fuels has also been



Scheme 1.1 Diagram illustrating the global dependency on fossil fuels for the USA within the overall energy supply sector and where each supply source is primarily consumed. Reproduced from Ref. [6] permission from Elsevier

fundamental for the population boom of the twentieth century. They made possible the diffusion of the energy intensive atmospheric nitrogen fixation into artificial fertilizers, contributing to the rise of intensive agriculture. Commodities such as wheat, corn, rice, and meat became progressively less expensive. At the same time agriculture itself became more and more demanding in terms of resources consumption.

Fossil energy sources are finite. This fact poses severe limitations to future economic development. The expanding world population, together with the rising standards of living, continuously pushes up the demand for energy. Energy hungry developing countries are putting increasing pressure on the continuous diminishing fossil fuel resources, making them even more costly. In 2005, oil consumption was approximately 1,000 barrels per second [1]. Just to give a rough idea this corresponds to 2 liters per person/day if we average over the population living on the Earth [2]. The current global power consumption sits around 13 terawatts (TW) and projections of energy consumption indicate that the demand could rise dramatically even in the very near future.

The problem of the exhaustion of fossil resources has been an intense subject of investigation starting from the second half of the twentieth century. Marion King Hubbert [3] proposed in the 1950s that the production of resources, particularly oil, would follow a "bell shaped," symmetric curve. The curve shows clearly a peak (Fig. 1.1).

He came to this conclusion by the analysis of the prototypical case of crude oil in the United States and, specifically, in the lower 48 states (US 48). By extrapolation, Hubbert was able to predict that the peak year for oil production in the US 48 would have been 1970. Indeed that was the case. Today, Hubbert's model is well known and has been applied to the whole world's oil production, (e.g., see [5]. According to the estimation, the global production peak is expected to occur

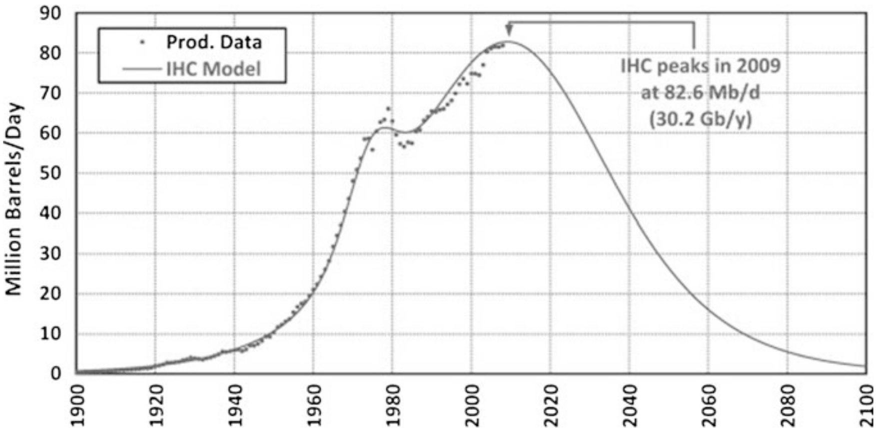


Fig. 1.1 A case of Hubbert "bell shaped" curve. Global oil annual production and its extrapolation to 2100. Reproduced from Ref. [4] with permission from Elsevier

within the first two decades of the twenty-first century (Fig. 1.1). While there may be uncertainties about the exact peak time, it is clear that the fossil fuels resources will, sooner or later, become scarce.

A Hubbert behavior has been found also in the production of coal and minerals. Some biological resources such as whale oil in the eighteenth century and Caspian caviar in the twentieth century have been shown to follow the same behavior see e.g. [7]. These findings suggest that Hubbert's model can be applied to all those resources for which the production rate is much faster than regeneration. This concept gives us the opportunity to introduce a definition of a renewable resource. Indeed we could define renewable resources as those resources able to regenerate at a rate larger than their consumption.

The general applicability and occurrence of bell-shaped production curves for the production of all sorts of nonrenewable resources has profound implications. From the Hubbert lesson we may learn that there is no way to plan a long-term "sustainable" economy if we focus on fossil resources alone. Production peak of fossil resources marks a critical moment in a economic system which is geared to maintain its growth forever and we may expect it to seriously affect the whole world's economy. It is hard to underestimate the importance of these concepts.

Not only is oil finite but also minerals and among minerals, those containing noble metals are the most likely to show scarcity in the near future. This is a matter of concern. Indeed these elements are essential in our technology and any effort that can be made to reduce their use is definitely worthy. A prototypical example is platinum which is essential in catalysis and, at present, is still the most relevant electrocatalyst for low temperature fuel cells. Platinum is a precious metal, hence it is scarce, hence has to be used with attention and if possible alternatives have to be developed. There will be no future for fuel cells and the hydrogen economy if we will not be able to reduce the platinum content in such devices. Nanotechnology is expected to play a key role in addressing this task, offering the chance to lower the noble metal loading also leading, in some cases, to its complete elimination (Fig. 1.2).

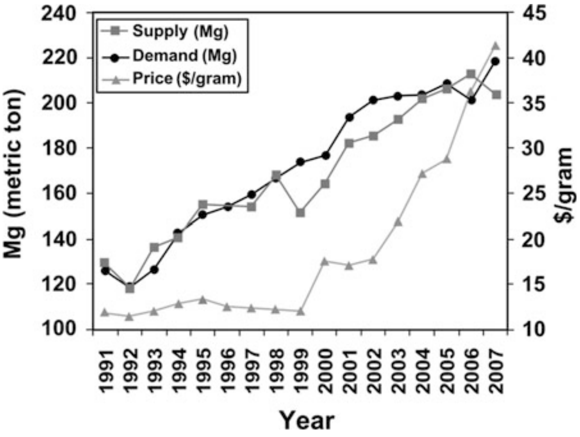


Fig. 1.2 Platinum supply, demand, and price. (Compiled from annual reports on platinum supply, demand, and prices published by Johnson Matthey Plc., and Kito.com.) reproduced from Ref. [8] with permission from Elsevier

1.3 Environmental Concerns

Finiteness is just one of the “bad sides” of fossil resources. The potentially damaging environmental effect of continuous carbon, natural gas, and oil usage has also to be seriously considered. CO_2 emission resulting from fossil fuel combustion has been shown to be the most relevant cause of the anthropogenic “greenhouse effect.” For this reason the burning of fossil fuels has been recognized as a primary cause for global warming. Global warming may result in significant changes to ecosystems. Its implications are still difficult to predict accurately and its consequences on humanity and the entire ecosystem could be, potentially, catastrophic. The global climate change issue is indeed on the agenda of both national and international institutions.

The exploitation of fossil fuel resources is a source of further relevant health and environmental hazards. Such risks are linked to virtually any stage of the life cycle of the resource, from extraction, to transportation and storage. Coal, oil, together with its derivatives, and methane burning results in the release of serious pollutants as effluents in the atmosphere, on the land and in water. Among the most notable and ubiquitous pollutants we may cite: CO, CH_4 (also relevant as a greenhouse gas), NO_x, SO_x, volatile organic compounds (VOCs), heavy metals, particulate matter (PM) and, as previously stated, very large quantities of carbon dioxide (CO_2). A vast variety of epidemiology investigations show that environmental pollution significantly increases the risk of contracting cancer and other pollution-related pathologies. This risk is nowadays considered unacceptable by the population. The rise of awareness in the public is pushing governments to deliver year after year more stringent regulations on pollutants emission. Ultimately new regulations might even result in the impossibility of applying certain technologies, imposing the transition to alternatives.

The development of electrochemical technology for energy conversion and storage offers us the chance to address directly some of these issues. Among other topics the electrochemical conversion of CO_2 into organic compounds, which in turn can be used as fuels, is of primary importance. This is an outstanding opportunity to mitigate the impact of fossil fuels on “greenhouse emissions.” At the same time this is indeed an extraordinary difficult challenge for electrochemical science and technology. Nanotechnology does offer the chance of designing materials on which devices can be built capable of addressing the targets for the proposed technology.

1.4 Renewable Energy Resources

Planning a sustainable future is now a priority. The development of new energy supply able to meet the demands for consumption in sectors such as household, commerce, industry, and transportation is a challenge that cannot be eluded. This must be done without impacting on the environment also assuring a long-term stability of the supply. There is no magic formula allowing the transition to such an energy sustainable system. Rather a mix of renewable energy sources is probably the best solution. What has to be common to all the possible power sources is the fact of being renewable.

Common applications of renewable energies are electricity generation and production of fuels for transportation. Nowadays, it is recognized that renewable energy has the potential to replace fossil fuels. Nevertheless such a change implies a system transition, requiring major technological changes and ultimately huge capital investment. Indeed and interestingly the variety of potential renewable energy resources offers the possibility to tailor the energy production according to local conditions (e.g. Iceland is not ideal for using photovoltaics due to its latitude, but it is exceptional in terms of geothermal energy for the geological nature of the island). The diversification of renewable energy resources [9, 10] hence provides a unique opportunity to create an energy system where the supply is not concentrated. In history concentration of essential resources has been proved to be risky due to geopolitical instability of the countries owning the resources.

Just to prove that renewable energy could, in principle, "power the world" we may analyze the case of solar energy. The radiation coming from the Sun and reaching the earth's surface is indeed the most abundant renewable resource available. In one year, the Sun delivers energy exceeding by a factor of 10,000 the energy consumed by humanity in the same time span. The problem arises in how we may efficiently collect it.

Let us go back to oil for a moment. One of the fortunes of oil is that it is found in oilfields, where it is (or better was) abundant and easy to extract. At the very beginning oil collection was an extraordinary straightforward task, providing large amounts of energy easy to transport and store with little effort. In terms of economy that was a huge opportunity for investment. While solar energy is and will definitely be more abundant than the energy from oil and other fossil resources, nevertheless, it suffers from the drawback of being diffused (we have seen that this has some advantage in terms of stability of the supply). This fact implies the need of a considerable amount of land to be used to recover it. Furthermore, the energy produced has to be stored and transported. That was easy with oil, but will be somewhat more troublesome with solar. This implies a complete rethinking of the energy system introducing new and clean technologies not only for energy harvesting, but also for storage transportation and conversion.

A large variety of renewable resources can be used for energy production. Here there is a short and somewhat arbitrary list, reporting some of the most popular approaches:

(1) Sunlight (converted into heat or electricity respectively by solar thermal or photovoltaics).
(2) Wind (to be converted into electricity by wind turbines or other mechanical devices).
(3) Hydroelectric (the mechanical energy of water can be converted into electrical energy by water turbines).

(4) Tides (mechanical energy of tides can be converted into electric energy).
(5) Geothermal heat (the heat contained in the earth crust can be employed in the production of vapor. The energy of the vapor can be then converted into electrical energy with turbines and alternators).
(6) Biomasses (photosynthesis provides CO_2 fixation in plants, which in turn can be burnt to render energy in the form of heat. The heat can be converted into electrical energy. Recently, direct conversion of biomass-derived compounds in fuel cells has been proposed).

Apart from tides (originated by gravitational interaction) and geothermal (originated by earth′s internal heat), all the other energy resources are the result of the impact of solar radiation onto the atmosphere. Wind comes from atmospheric thermal convection, biomasses result from the radiation promoted CO_2 fixation, and hydroelectric from the rain which is due to water evaporation provoked in lakes, seas, and rivers by the heating induced by the absorption of solar radiation.

Solar radiation can be converted into electricity, either directly using photovoltaics (PV), or indirectly using concentrated solar power (CSP) [11, 12]. PV has experienced an outstanding commercial growth in the last decade, providing the opportunity of realizing a distributed energy generation system. Even large PV fields have been established. PV is now a solid reality in the renewable energy panorama and its growth is expected to continue in the future.

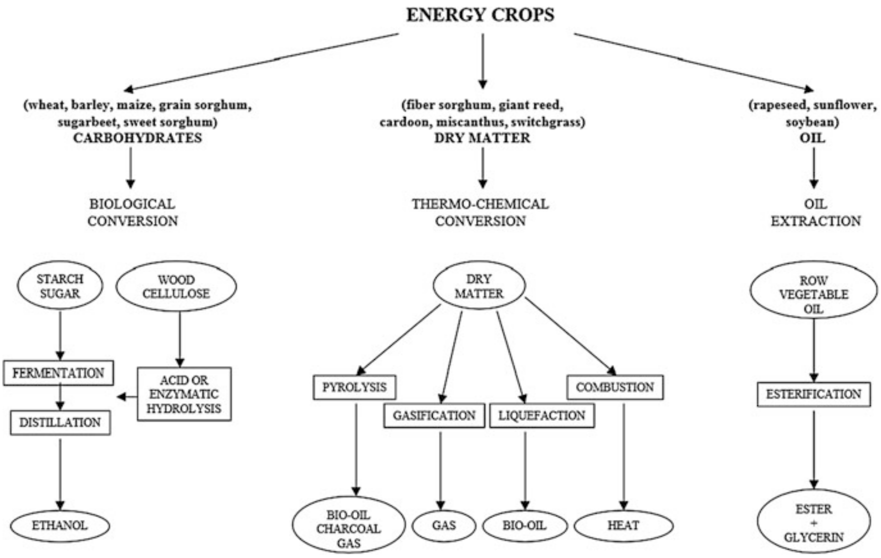
A significant issue connected with most of the renewable energy technologies is the intermittent nature of energy generation. While a power plant fuelled with fossil resources can produce more or less on demand, this is not true for, e.g., of PV or wind energy. Energy production occurs as a result of local environmental conditions. Sometimes the production is not easy to forecast, producing difficulties in the electric grid management. As a result of this there is a huge demand for energy storage systems for buffering the electrical energy production from renewables. Coupling PV with electrolysis for the production of H_2 is in principle a solution. This would support the development of the so-called hydrogen economy that will be discussed later on. H_2 can then be exploited in fuel cells for transportation or even for producing electrical energy on demand in stationary systems. This is straightforward to understand. But it has to be pointed out that each energy conversion process leads to energy loss. Again, nanotechnology may lead to the synthesis of materials with improved electrocatalytic performance, leading to highly energy efficient processes potentially capable of improving the energy efficiency of a renewable energy-based economy.

An interesting alternative to solar energy storage is the CO_2 fixation into organic compounds through the photosynthetic biomass production (Scheme 1.2). Biofuels such as ethanol, biodiesel, and biogas [13] can be considered as the carriers of solar energy. This point is considered in this book. Indeed a variety of the nanostructured materials presented are aimed at the direct conversion of biomass derived compounds into electrical energy. Among such compounds a very special place is occupied by ethanol, which, when derived from biomasses is often referred to as “bioethanol.” It is obtained mostly from sugars which are contained in corn [14], sugarcane [15], or sugar beet [16]. Recently the possibility of obtaining ethanol and other bio-alcohols from cellulose has been deeply investigated. This has led to the possibility of producing hydrogen by steam reforming of bioethanol obtained using portions of land not previously devoted to food production [17]. This is an essential issue, as a sustainable future cannot accept a competition between energy production and the human food energy chain. Subtraction of land from food production would especially damage less developed countries, with scarcity in essential commodities.

Biofuels can be directly burned in internal combustion engines. This is true for bioethanol and for biodiesel especially [18]. Nevertheless, combustion, even if performed with biomass derived compounds, is a source of pollution even if not a "greenhouse" contribution anymore. Whenever possible a direct, low temperature, conversion of the energy contained in biomass-derived compounds into electrical energy (e.g., through alcohol oxidation in direct alcohol fuel cell [19–22]) would definitely be advantageous for the environment.

At present the common problem of renewable resources, apart probably from hydroelectric, is that they are still not competitive in terms of produced energy prices with the nonrenewable resources. Technology is by the way quickly evolving and as many of the illustrated approaches have reached mass production, the cost of production is lowering (Scheme 1.2).

The relatively high prices of renewable energy requires a governance directed by major political institutions, with the target of setting up long-term strategies aimed at moving to a fully energetically renewable system. This has been done in a



Scheme 1.2 An example of biomass exploitation. Main energy crops, conversion processes, and available products for energy uses. Reproduced from Ref. [23] with permission from Elsevier

variety of cases. PV has been recently extensively supported by economic incentives to its installation and consequent energy production.

1.4.1 The EROEI and the Life Cycle Analysis

In the previous chapters we have defined the concept of renewable. While this concept is pretty straightforward to understand, it is worthy to dedicate some room to the way that is currently in use to establish and quantify the energy impact of such technologies.

Thermodynamics states that the exploitation of an energy resource can never be 100 % efficient. For instance, before recovering the chemical energy stored in oil, we must spend some energy in a variety of operations which include: (i) prospecting; (ii) drilling; (iii) extracting; (iv) processing, and (vi) transporting. The concept of EROEI (energy return for energy invested) allows us to quantify all of these contributions and can be used to understand if the exploitation of a resource is convenient or not. Furthermore, it can tell us the amount of energy that the resource can return as compared to the energy we spend to recover it. In the end the EROEI can be defined as "the ratio of the energy obtained from the resource to the energy expended in production" [24–26]. Alternatively, one could consider the concept of net energy (in practice the energy gain) which is defined as the energy produced minus the energy expended by the resource. The relation between the two quantities is the following: if EROEI is equal to 1 or lower, the net energy is 0 or lower, while when the EROEI is larger than 1 the net energy gain is larger than 0. EROEI values up to 40 and more have been reported for oil [27].

The larger the EROEI the more preferable the resource exploitation. This is true in principle. However, in practice, some processes have been carried out even at low EROEIs, sometimes even smaller than 1. This has happened as a result of specific choices of political and economic systems. The most notable example is probably the production of biofuels from corn and in particular ethanol. Detailed analysis has shown that this process has a very low EROEI [28, 29]. Interestingly, according to the Pimentel and Patzek analysis bioethanol production from corn may lead to a use of energy from fossil fuels larger than the energy contained in the resulting biofuel. Nevertheless, the US government decided to proceed providing substantial financial aid to support the activity. Production from switchgrass, lignocelluloses, rapeseed, and sugarcane has been proved to be much more efficient with EROEI in some cases larger than 10 and those are, in the opinion of these authors, the future of biomasses.

The calculation of EROEI may be a difficult task. Many factors and boundaries need to be accounted for. These aspects may be considered according to the "Life Cycle Analysis" (LCA) concept. LCA is a well-established approach. Standards defining protocols for performing the analysis have been elaborated (e.g., ASTM E1991-05 [30]).

It is now worth looking at how the life cycle of a product is performed. LCA attempts to include all stages of a product's life in an evaluation. In doing this it considers that all these aspects are interdependent, leading one operation to the next. Hence LCA provides a comprehensive view of the environmental aspects of all the stages involved in the product realization. Next a list of the main aspect usually considered in the LCA is reported:

- collection of all the significant energy and material inputs and the associated emissions to the environment;
- evaluation of the potential environmental impacts associated with all inputs and emissions;
- results, analysis, and reporting for decision making.

The collection of relevant information requires both input and output. The following elements are usually accounted for:

- Input
  - Raw materials;
  - Manufacturing;
  - Use/reuse/maintenance;
  - Recycle/waste management.
- Output
  - The products;
  - Atmospheric emissions;
  - Waterborne wastes;
  - Solid wastes;
  - Co-products;
  - Other releases.

LCA can be extended to the analysis of energy and to the definition of the EROEI of energy resources or for the evaluation of the energy efficiency of energy conversion systems. These considerations lead to the life cycle energy analysis (LCEA). LCEA accounts for all energy inputs as well, not only the direct energy inputs during manufacture, but also those needed to produce components, materials, and services needed. With LCEA, the *total life cycle energy input* is established. This approach is now spreading amongst the researcher community. Extensive evaluations have recently been undertaken in Europe, China, US, and especially the UK to determine the life cycle energy (alongside full LCA) impacts of a number of renewable technologies [31].

We believe that being aware of the existence of the concepts of EROEI and net energy as well as of the LCA and LCEA is fundamental for both researchers and professionals involved in the field of synthesis and the application of electrocatalytic materials for electrochemical energy conversion and storage. Such evaluations are usually meaningless, if not impossible, at the research lab stage. But it is important to stress that a well performing material is not the whole story. Even the nature of the material, its manufacturing, the use that it makes of resources can play a determining role in defining whether its exploitation in technology is profitable or not. When considering material design criteria it could be a good exercise not to think of the material functionality alone but also to consider resource-related aspects. This is important in a modern context where research is often asked to follow directions indicated by institutions and formulated to give answers to specific needs of society.

1.4.2 The Role of Hydrogen and Energy Vectors

Energy alone means nothing. Society needs energy in the right place at the right time. This is especially true for transportation. The automotive sector needs reliable energy storage systems capable of delivering the required amount of power on demand. Hydrogen has been proposed as the energy carrier of the future as, in principle, it is applicable as a fuel for transportation and an intermediate in the conversion of renewable energy sources.

Hydrogen that is produced mainly by steam reforming of methane is used primarily to produce NH_3 which in turn is transformed into urea, and then in fertilizers. Hydrogen can be exploited in an internal combustion engine, but this is not the best solution. Internal combustion engines suffer from the thermodynamic efficiency limitation of thermo-mechanical cycles; furthermore the high temperature produced by the combustion of hydrogen with air, apart from heat and water, may release nitrogen oxides which have been recognized as extremely hazardous pollutants.

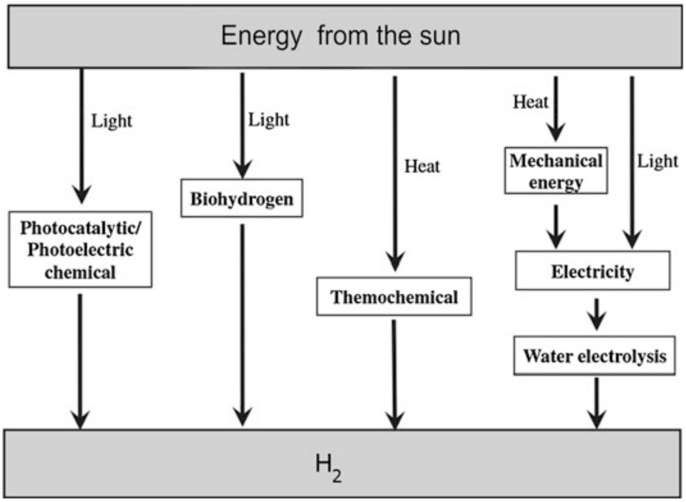
The combination of molecular hydrogen and oxygen in a fuel cell is a cleaner opportunity to generate electricity only resulting in the release of heat and water into the environment. Coupling hydrogen with low temperature fuel cells gives the opportunity to make the transportation sector energetically and environmentally sustainable. By the way, there are a variety of challenges that need to be considered before hydrogen can become a commercial reality for energy storage. First, of all hydrogen does not form spontaneously, at least in the large amounts potentially required by our society, it has to be produced. Doing this in a clean and efficient way from chemical compounds requires energy [32–34]. Indeed this is the reason why hydrogen is not an energy resource, but just an energy carrier.

At present most of hydrogen production employs fossil fuels both as energy and as hydrogen sources. Such methods require high temperatures to be effective. Reforming processes from fossil fuels result in what is usually called “syngas” which is a blend of CO and H_2. This is a drawback for fuel cell applications, as CO is a serious poison for platinum electrocatalysts. Hence, after hydrogen synthesis a further purification of the syngas from CO has to be performed. Lastly, reforming is not carbon dioxide neutral, contributing to the rise of CO_2 concentration in the atmosphere and ultimately to the increase of the “greenhouse effect.”

To fulfill the requirements for a sustainable energy carrier, hydrogen has to be produced from water using renewable energies (such as solar energy). A scheme summarizing the possible ways to sustainably produce hydrogen is reported in Scheme 1.3 [35]. Hydrogen production from renewables is a concrete chance for the future and it has been hypothesized that the optimal endpoint would be the setup of a "Hydrogen Economy" Hydrogen economy should replace fossil fuels with hydrogen produced from renewables. Many environmental advantages will result from the Hydrogen Economy, and as such, it can be referred to as the Hydrogen Environmental Economy.

Criticism has also been expressed toward the concept of hydrogen economy based on its overall energy efficiency. It has been pointed out that hydrogen has to be made from renewable electricity by the electrolysis of water and then its chemical energy has to be converted back into electricity with fuel cells. Fuel cells efficiency maximum ranges around 50 %. Moreover, there are problems related to the storage technology [36] and to the creation of a safe distribution and transport network for this new energy carrier. When delivering hydrogen, whether by truck or pipeline, the energy costs are several times that for established energy carriers like natural gas or gasoline.

Biomasses conversion into fuel could be an interesting alternative to hydrogen as an energy carrier, even if more demanding in terms of catalysis. Bioethanol and other biofuels are liquid, with high energy density and easy to store and transport. In such a sense they are appealing, at least in principle, for powering automobiles. The efficiency of energy conversion in direct alcohol fuel cells is still not sufficient for powering cars or trucks. Nevertheless, it is the opinion of the authors that there is huge room for the development of such devices. Electrocatalysis is the main issue here and we expect that the ability to manipulate matter at the nanoscale holds the key to increasing the energy efficiency of such devices.



Scheme 1.3 Hydrogen from solar energy; production processes

1.5 Fuel Cells as Power Sources

A fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen [37]. Other oxidizing agents could in principle be used but their application is limited to very specialized niches. Hydrogen is the most commonly employed fuel in fuel cells, but hydrocarbons such as natural gas and alcohols like methanol and ethanol are also being used. Direct Alcohol Fuel Cells (DAFCs) have attracted increasing interest over the past decade, with a special emphasis on alkaline devices [38]. Easy storage and handling, high energy density, and wide availability are features that make alcohols attractive liquid fuels for the most promising alternative power sources for transportation, portable electronics, and stationary applications.

What makes fuel cells so appealing is the fact that they generate electricity through electrochemical processes, rather than combustion. Typical fuel cells consist of an anode (negative side), a cathode (positive side), and an electrolyte that allows ions to move between the two sides of the fuel cell (a detailed description of the fuel cell structure and components is deferred to Chap. 3). The energy efficiency of fuel cells is generally between 40 and 60 %. Values up to 85 % may be obtained if heat recovery systems are used. Figure 1.3 reports the main classes of fuel cells. They include: alkaline fuel cells (AFC), proton exchange membrane (PEM) fuel cells, direct alcohol fuel cells (DAFC), molten carbonate fuel cells (MCFC), phosphoric acid fuel cells (PAFC), and solid oxide fuel cells (SOFC). While these technologies are not yet mass technologies, some of them have been exploited at the commercial level. Each of these technologies has its own characteristics, such as different operating temperatures, catalysts, and electrolytes. The operating conditions of fuel cells define its range of application.

In this book we will limit our discussion to low temperature fuel cells and among them to the polymer electrolyte membrane fuel cells. Electrocatalysis in this category of fuel cells is particularly demanding and nanotechnology has the potential to dramatically improve the energy performance and feasibility of such devices.

Why direct chemical energy conversion into electricity in fuel cells is potentially so relevant? First, we know they are functional to the hydrogen economy. But there is more. Fuel cells have many potential benefits against competing technologies. Among them we cite the usually high efficiency, their modular nature which make fuel cell power units suitable for scale-up. A somewhat detailed list of major fuel cell advantages is reported below:

(1) Low-to-Zero Emissions and High Efficiency:
    Fuel cells especially in low temperature technologies such as those based on polymer electrolyte membranes only emit neglegible amounts of hazardous effluents. Furthermore, the fact they don't use thermomechanical cycles is an advantage in terms of thermodynamic efficiency.
(2) Fuel flexibility and connection to sustainable development:
    Fuel cells are a key element in the hydrogen economy and sustainable

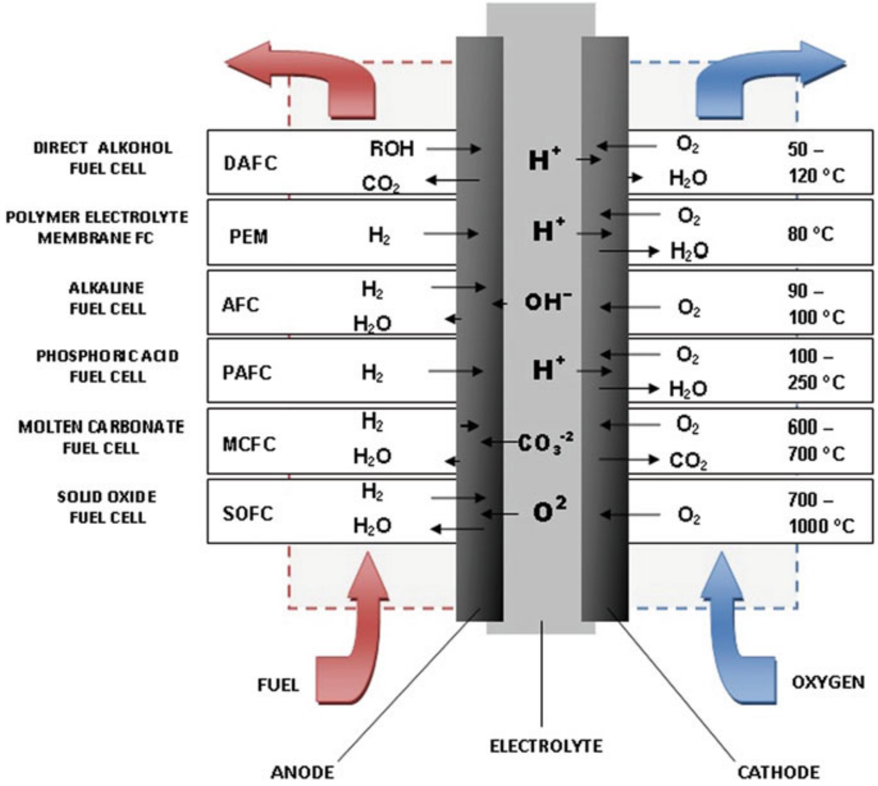


Fig. 1.3 Typical fuel cells consist of an anode (negative side), a cathode (positive side), and an electrolyte that allows charges to move between the two sides of the fuel cell. Adapted from Ref. [39] with permission from Elsevier

development based on renewable energy resources. As stated in the previous sections they may employ a variety of fuels such as hydrogen but also alcohols and organic compounds derived from biomasses. Solid oxide fuel cells may also directly employ hydrocarbons, without the need for using precious metal electrocatalysts.

(3) Reliability and Energy Security:
Practical applications need to rely on constant power to maintain operations. Buildings require power that is available practically without discontinuing service operations (e.g., hospitals). In some areas the electrical grid cannot guarantee such continuity of the service. Fuel cells can supply power independently of the grid. They can act as backup power to a grid-connected building. Fuel cells can also be configured to be a building's primary source of power (e.g., SOFC). Fuel cells can also be located in extreme climates, and rural areas where the grid may not be present and transportation is difficult due to the lack of infrastructure [39].

(4) Durability:
Without any important mechanical parts fuel cells may in principle be suitable candidates for power generation with low maintenance and durable operations. By the way for demanding applications such as automotive, fuel cells still do not meet the durability targets, but there are chances that this will happen in the near future as indicated by the US Department of Energy. Fuel cells are in principle also suitable for portable power electronic devices such as laptops and cell phones. For these applications fuel cells may exhibit much longer service life as compared to batteries, and since fuel cells have a higher energy density, they offer the chance to realize higher power sources. Furthermore, no electric grid is required as only the replacement of the fuel load is required. The recharging operation is also much shorter than that of batteries.

1.6 Electrolytic Hydrogen Production

The "hydrogen economy" calls for efficient processes for the production of hydrogen from renewables. Electrolytic water splitting (water electrolysis) is, at present, the technology that best matches the requirements for hydrogen production from renewable energy sources. While fuel cells have not yet been fully exploited commercially, electrolysis is in some sense a more mature technology and has been widely applied to the production of pure hydrogen. Electrolyzers in a wide variety of sizes are available and it is easy to find them in research labs around the world utilized for in situ hydrogen production. Electrolytic hydrogen production accounts for approximately 1 % of the overall hydrogen production in the world.

What makes electrolysis particularly appealing in terms of sustainability is its ability to directly convert electric energy into molecular hydrogen. So, any possible renewable source of electricity may be used to drive electrolytic hydrogen production, leading to a valuable system for storing energy from intermittent sources. The energy consumption for hydrogen production with state-of-the-art technologies is around 50 kWh kg^{-1} of molecular hydrogen of which 33.6 comes from thermodynamics (1.23 V is the standard thermodynamic potential). The rest comes from a variety of contributions, including the activation potential for the hydrogen and oxygen evolution reactions. Such contributions may be lowered by using better electrocatalysts whose performance can be tuned by using nanotechnology.

As an alternative to traditional water electrolysis the introduction of sacrificial agents in the anode compartment may provide large energy savings [40–42]. Water can be substituted at the oxygen evolution electrode (anode) with an easily oxidizable species such as, for example, ammonia or ethanol, at which point oxygen is no longer evolved at the anode. The uses of such easily oxidizable species as sacrificial agents allows us to reduce the thermodynamic contribution to values close to 0 V. Under these conditions it has been shown that electrolysis may occur at potentials lower than 1 V [41], leading to large energy savings. If the sacrificial agents are produced from biomasses with processes having large EROEI such a process may be advantageous with respect to conventional electrolytic technologies. It has been shown that from electrolytes containing ethanol hydrogen can be produced with electrical energy consumptions lower than 20 kWh kg^{-1}. As by-products organic compounds with high added value may also be obtained and this could contribute to the profitability of the process.

1.7 CO_2 Electroreduction

The steady increase in atmospheric CO_2 concentration is a pressing global environmental issue; as a consequence the electroreduction of carbon dioxide is currently investigated by many scientists as a one of the most promising ways to convert waste CO_2 into useful organic compounds which can be used as fuels or raw chemicals [43]. The field of electroreduction of CO_2 is by the way far less mature than fuel cells or electrolysis. No commercial application is actually known, but there is truly a huge interest in the subject. The task is by the way extraordinarily difficult. The main reason is due to the exceptional stability of CO_2 which requires a lot of energy for its activation. CO_2, according to thermodynamics, is more stable than any other organic compound in our atmosphere. Furthermore, the reduction mechanism requires the formation of a radical species whose activation potential is -1.9 V against the standard hydrogen electrode (SHE) [44]. Hence, CO_2 reduction in electrolytic devices requires a very high electrical energy input which is mostly related to the cathodic reduction of CO_2. There is hence great potential to improve the energetic performance of devices for CO_2 reduction to fuels concentrating on the cathode electrocatalyst. Material science and nanotechnology are expected to contribute massively to this subject resulting in improvements in the energy efficiency and compound selectivity through the design and realization of nanostructured electrode architectures.

1.8 Electrocatalysis and the Need for Nanotechnology

All the devices and processes covered by this book make use of electrocatalysts to enhance energy efficiency. Electrocatalysis is the branch of electrochemistry devoted to understanding and modifying reaction mechanisms through the use of catalytic materials. Electrocatalysis is a very old science. According to Jaksic et al. "…electrocatalysis and the search for promising electrocatalysts effectively started its development after two distinct core discoveries in the science: (i) Sir William Grove's inventive discovery and theoretical definition of (H_2/O_2) fuel cells and their fundamental structure in 1842 and (ii) Tafel plots in the year 1905, when various metals were distributed and ranged on the $\eta = \mathrm{a} - \mathrm{b} \log \mathrm{j}$ coordination chart, with clear distinction amongst good and bad, or, on more or less polarizable, mostly transition elements or their composite electrode materials." [45] The development of new electrode architectures with enhanced electrocatalytic properties is a subject strictly connected to material science. The electrocatalytic properties of electrodes can be tuned by acting on a variety of material characteristics; the most relevant aspects connected to the electrocatalytic activity are:

(1) Composition;
(2) Surface structure;
(3) Morphology.

All of these elements together determine the ability of a given material to accomplish a given task. In electrocatalysis a smart design of a material can have the huge payback of improving the rate of a given electrochemical reaction with positive impact on the energy efficiency of the processes. We will not give here a complete description of how these aspects relate to the electrocatalytic activity as they will be extensively considered in Part 1 chapters.

There is still one important element which has not been explicitly considered yet and that may be considered the true reason for advocating nanotechnology in electrocatalysis. This is the surface area of the catalyst. The importance of this aspect resides in the nature of electrochemical reactions. Electrochemical reactions typically occur at the surface of an electronically conductive material (the electrocatalyst) which is in contact with an ionically conductive medium containing the electroactive species. According to this consideration and from the fundamentals of electrochemistry it is known that the energy absorbed by a given electrochemical reaction to proceed at a certain rate decreases as the extent of the electrode–electrolyte interface increases. Hence the exploitation of spontaneous electrochemical reactions (e.g., hydrogen or alcohols oxidation or oxygen reduction) in devices requires the electrode electrolyte interface to be as large as possible. Basically, the surface of the electrocatalyst has to be as large as possible and this is possible introducing in the material features with a scale length of the order of a nanometer. Indeed the success of polymer electrolyte fuel cells in the conversion of hydrogen chemical energy into electrical power is largely due to the availability of high surface area platinum electrocatalysts. The carbon supported platinum nanoparticles of the catalyst layer shows diameters ranging well below 10 nm and are employed both as anode and cathode. To go a bit more in detail, in PEMFC systems electrocatalysts with a metal loading of a fraction of mg cm^{-2} are employed. This is because platinum is rare and we do not want to waste it. The platinum specific surface area of such catalysts may range even over 100 $\mathrm{m}^2\ \mathrm{g}^{-1}$ [46]. Just to have a rough idea this means that with 0.4 g we would be able to cover a 40 m^2 floor with platinum. What would be the thickness of the floor? Very small indeed, just in the nanometer range. In turn the metal loading in a fuel cell electrode could be in the range of 0.1 mg cm^{-2}. This means that an electrode with a section area of 1 cm^{-2} would show a real catalyst area of 100 cm^2. With just