Energy Generation and Storage

DOI: 10.1002/anie.200903603

Electrochemical Versus Heat-Engine Energy Technology: A Tribute to Wilhelm Ostwald's Visionary Statements

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Carnot process · electrochemistry · energy technology · fuel cells · heat engines

Dedicated to Wilhelm Ostwald

1. Introduction

Our present situation concerning major fossil energy carriers and energy consumption is characterized by limited reserves and resources, along with emission problems considering crude oil, natural gas, coal and uranium as primary energy sources. At the same time, the worldwide demand for electrical energy has increased from 8.3 million GWh in 1980 to 18.9 million GWh in 2006, and is estimated to further increase to 30.7 million GWh in 2030.

Energy management is a rather complex problem. Increasing contributions of renewable energies, such as wind, solar, and wave power, tend to complicate the grid management. Therefore, generation of electrical energy is only part of the challenge. The management and storage of electrical energy will become essential to maintain the present grid quality.

Energy conversion processes today are under special consideration because of two factors associated with them, namely the limited availability of primary energy carriers and the emission of pollutants, with inherent local and global negative effects on the environment. Energy conversion processes that aim at generating electrical power reveal efficiencies not much higher than 30%, which indicates that losses in form of heat or chemical substances amount to more than two thirds of the primary energy. Conventional processes, for example those in a heat-engine-based power plant, are volume processes, such as combustion, which results in mechanical and then in electric energy. By contrast, other technologies, such as photovoltaics or electrochemistry (batteries, fuel cells, or super caps), are based on interfacial transfer of energy and/or charge. In contrast to the performance of heat engines, which is limited by the Carnot efficiency, interfacial reactions are usually of much higher thermodynamic efficiency.

The purpose of this essay is to critically compare Carnot-based and electrochemical methods that are used for the generation and storage of energy, and to reflect advantages and disadvantages of both alternatives. One of the first scientists who was aware of the impact and the importance of energy conversion and storage devices based on electrochemical interfacial reactions was the Nobel Laureate Wilhelm Ostwald (1853–1932), who was at the time professor at the first chair of physical chemistry at the University of Leipzig. The view of Ostwald and what is today's understanding of energy conversion will both be apparent in this essay, in order to reflect the development of the opinion about this topic from the 18th century up to now and to rise important questions in this context.

2. Classical Heat-Engine Cycles

Thermodynamic considerations gave rise to the first heat engines, which were used to generate mechanical or electrical energy. Since the 18th century, conventional reciprocating steam engines have served as mechanical power sources, with notable improvements being made by James Watt. The first commercial central electrical generating stations in New York and London, in 1882, used steam engines.[1]

In 1894, Wilhelm Ostwald predicted a technical revolution caused by the fuel cell, which would eclipse the invention of the steam engine. Despite Ostwald's predictions however, the first-generation heat engines are still serving as power plants today. Further developments have lead to the introduction of combined-cycle power plants. Usually a combination of several cycles, operating at different temperatures, yield a considerably higher system efficiency. Heat engines are only able to use a portion of the energy (usually 35 to 41%). The remaining heat is generally wasted. In a combined-cycle power plant (CCPP), or combined-cycle gas-turbine (CCGT) plant, a gas-turbine generator produces electricity and the waste heat is used to make steam for generating additional electricity with a steam turbine. This last step enhances the efficiency for electricity generation to about 60%, because the temperature difference between the input and output heat

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levels is higher, leading to an increase in the Carnot efficiency. Most modern power plants in Europe and in North America are of this type.

If the waste heat of a conventional thermal power station is for example utilized to heat a district, it is called co-generation. This heat gives an additional efficiency of about 40–50%, which leads to an increase of the overall efficiency to about 90%. These engines use black and brown coal as fuel, or nuclear power.

In contrast to the stationary systems described above, mobile engines are needed in many energy production applications. The best known mobile engines are the four-stroke (Otto), Diesel, and Stirling engines.

The first patent for a four-stroke engine was by Eugenio Barsanti and Felice Matteucci in 1854, and the first prototype was constructed in 1860. It was conceptualized by the French engineer, Alphonse Beau de Rochas, in 1862. The German engineer Nicolaus Otto developed the first functioning four-stroke engine, and the four-stroke internal combustion cycle is thus often known as the Otto cycle. Today, internal combustion engines in cars, trucks, motorcycles, aircraft, construction machinery, and many others commonly use a four-stroke cycle. The four strokes are intake, compression, combustion (power), and exhaust, and occur during two crankshaft rotations per working cycle of the gasoline and Diesel engines. The cycle begins at top dead center, when the piston is farthest away from the axis of the crankshaft. In the intake or induction stroke, the piston descends from the top of the cylinder, reducing the pressure inside the cylinder; a mixture of fuel and air is drawn into the cylinder through the inlet port. The inlet then closes, and the compression stroke compresses the fuel/air mixture. In the case of a gasoline engine, the fuel/air mixture is then ignited near the end of the compression stroke by a spark plug. The resulting pressure of burning gases pushes the piston, resulting in the power stroke. In the exhaust stroke, the piston pushes the products of combustion from the cylinder through an exhaust valve (Figure 1a).[2]

The Diesel engine relies on self-ignition of the fuel/air mixture, and thus differs from the gasoline-powered engine in that it uses higher compression of the air to ignite the fuel instead of using a spark plug. Air is introduced into the combustion chamber, which is then compressed, thereby heating up to 550 °C. Fuel is then injected directly into the compressed air and forms small droplets. The heat of the compressed air vaporizes fuel from the surface of the droplets and the vapor is finally ignited. The name of the engine is derived from the German inventor Rudolf Christian Karl Diesel, who invented this engine in 1892. He originally designed it to run on coal dust, and also used various oils, including vegetable oils, as fuels.[3]

A Stirling engine converts heat energy into mechanical power by alternately compressing and expanding a fixed quantity of a gas at different temperatures. This engine, invented by Robert Stirling in 1816, was originally designed as an alternative to the steam engine; however it was largely confined to low-power domestic use. In recent years, the Stirling engine, which is compatible with renewable energy and fuel sources, has become more significant in light of

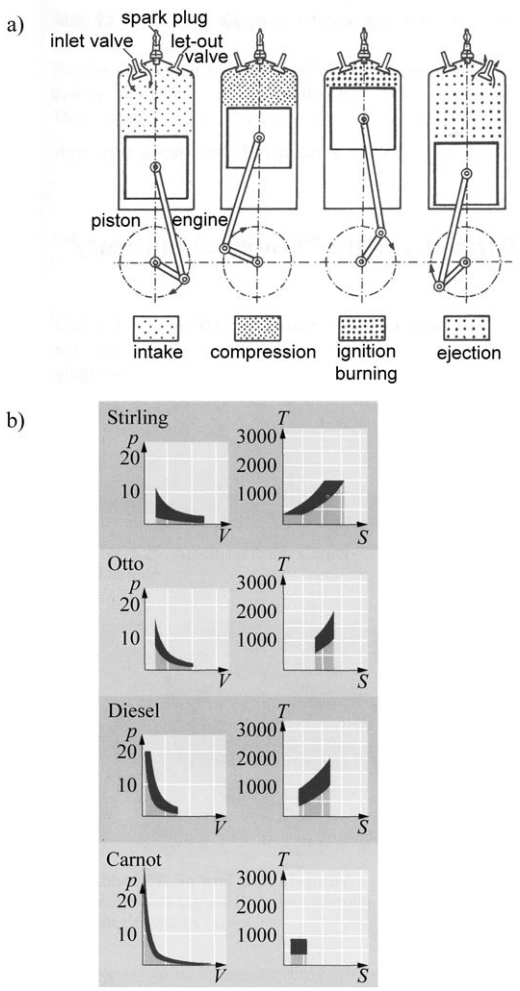

Figure 1. a) An internal combustion engine.[2] b) Working diagrams of thermal engines in *p*,*V* and in *T*,*S* forms. The *p*,*V* diagram shows the processes inside the piston; the work per cycle is depicted by the dark area. The *T*,*S* diagram shows the work (dark gray) and the lost energy (pale gray) directly.[4]

increasing fuel prices and concerns regarding oil availability. The Stirling engine is also very efficient, quiet, and makes good use of waste heat. It is a closed-cycle regenerative heat engine with a working fluid that is permanently in the gaseous state. As an external combustion engine, it isolates its working fluid from the energy input supplied by an external heat source. An internal regenerative heat exchanger increases its thermal efficiency to approach the limiting Carnot efficiency. The key component is the regenerator, which works like a thermal capacitor; its presence distinguishes this engine from any other closed-cycle hot gas engine. The theoretical efficiency of the idealized Stirling cycle equals that of the hypothetical Carnot cycle, that is, the highest efficiency attainable by any heat engine. However, a real Stirling engine is still far from being ideal.

The first criticism against heat engines, which related to their limited efficiency that is determined by the Carnot cycle, was expressed by Wilhelm Ostwald. Practical issues reduce the efficiency of steam engines, owing to limits of convective heat transfer and viscous flow (friction). There are also

mechanical considerations, for example, limitations imposed by the materials, such as non-ideal properties of the working gas, thermal conductivity, tensile strength, creep, rupture strength, and melting point.

Figure 1b shows working diagrams of thermal engines in p,V and in T,S form.[4] The p,V diagrams depict best the processes in a thermal engine, because the work given or consumed by the gas is directly visible as the area $\int p\,dV$. In a real engine, a rounded cycle is passed through in the p,V diagram, which can be composed of four parts of the typical lines, being the isotherm, the adiabatic curve, the isobar, and the isochor. In a gasoline engine, combustion heats the fuel/air mixture from T_1 to T_2. The hot gas then moves the piston adiabatically forward and cools down to T_3. After exhaust emission and intake of a fresh mixture at temperature T_4, the mixture is compressed by the piston, whereupon parts of the energy won before are lost again. This adiabatic compression heats the mixture to T_1, and the cycle can start from the beginning. In the Diesel engine, the upper corner of the Otto cycle is almost isobarically isolated. In the Stirling engine, the air contact alternates between a heat source and a water cooling device. In approximation, this leads to an isochoric increase or decrease of the pressure with a subsequent isothermal expansion or compression. In each working cycle, the gas performs work during the expansion, which is given by the area under the upper series of curves of the p,V diagram. Afterwards, the system must be brought back to its initial state by returning it an energy given by the area under the lower series of curves. The effective work is given by the difference, that is, the area inside the series of curves.

The ideal Carnot process is shown in more detail in Figure 2. It consists of two adiabatic and two isothermal cycles. In the isothermal cycles, the steam is in contact with

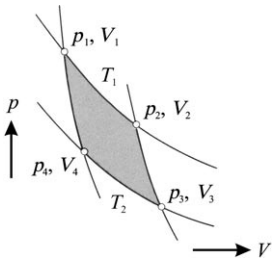

Figure 2. a) Carnot process. ($p_1,V_1 \rightarrow p_2,V_2$): isothermal expansion; ($p_2,V_2 \rightarrow p_3,V_3$): adiabatic expansion; ($p_3,V_3 \rightarrow p_4,V_4$): isothermal compression; ($p_4,V_4 \rightarrow p_1,V_1$): adiabatic compression.[4]

the combustion chamber T_2 or with the capacitor T_1. In the adiabatic cycles, the piston moves without heat contact. The efficiency of the Carnot cycle is a function of the temperatures T_1 and T_2. T_1 cannot be arbitrarily high owing to the properties of the materials, and $T_1 - T_2$ cannot be too large owing to heat conduction within the machine.

With the translational energy per mole gas being $^3/_2\,RT$, the power of a Carnot engine can be described as given in Equations (1) and (2), where T_1 is the temperature before compression and T_2 the temperature after expansion, with $T_1 > T_2$. The thermal efficiency can thus be calculated according to Equations (3a) and (3b).

$$W_{out} = {}^3/_2 R(T_1 - T_2) \quad \text{and} \tag{1}$$

$$W_{in} = {}^3/_2 RT_1 \tag{2}$$

$$\eta = \frac{W_{out}}{W_{in}} = \frac{(T_1 - T_2)}{T_1} \quad \text{or} \tag{3a}$$

$$\eta = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}} \tag{3b}$$

A fuel cell does not obey the rules of the Carnot process, which always limits the efficiency of thermal engines to a value far below 100%. As Wilhelm Ostwald predicted:

"The path which will help to solve this biggest technical problem of all, this path must be found by the electrochemistry."

"If we have a galvanic element which directly delivers electrical power from coal and oxygen (…), we are facing a technical revolution that must push back the one of the invention of the steam engine. Imagine how (…) the appearance of our industrial places will change! No more smoke, no more soot, no more steam engine, even no more fire (…), since fire will now only be needed for the few processes that cannot be accomplished electrically, and those will daily diminish."[5]

"… Until this task shall be tackled, some time will pass by. But that this does not concern an inefficient scientific idea, I believe however, to be able to assume."[5]

With both assumptions, Ostwald was entirely right.

3. Electrochemical Systems

3.1. Energy Conversion and Storage

Electrochemical systems can be employed nowadays to generate and to store energy as an alternative to the conventional Carnot-based heat engines. Important electrochemical energy-conversion processes are found in batteries and fuel cells, and energy storage is incorporated by employing rechargeable batteries, supercapacitors, generation of hydrogen by electrolysis, and generation of methanol from electrochemically generated hydrogen and CO_2/CO-containing syngas. Heat-engine cycle processes are volume processes, whereas all electrochemical systems that are used for energy conversion and storage are based on reactions that take place at an interface. This makes them dependent on the surface morphology and its physical and chemical properties.

A battery or voltaic cell consists of one or more electrochemical Galvanic cells that store and convert chemical energy into electric energy. Since the invention of the first Voltaic pile in 1800, the battery has become a common power source for many household and industrial applications. The name "battery" was coined by Benjamin Franklin for an arrangement of multiple Leyden jars, an early type of capacitor.

Wilhelm Ostwald saw the need to store energy in the smallest available space. He described the importance of using batteries as electrochemical storage devices when he wrote: *"Another important thing is the question about accumulators, that is, about the best storage of electrical energy. We have to solve the problem of storing a maximum of energy in a preferably small room with low weight"*.[5]

Ostwald's idea to store electrical energy in a battery was revolutionary at that time. He was so passionate about it that he named his house in a town called Grossbothen "Landsitz Energie", which means "energy cottage".[6]

Different types of batteries include non-rechargeable batteries (primary batteries), in which chemical energy is stored internally and the discharging reaction that takes place at the electrode/electrolyte interface is irreversible, and rechargeable batteries or accumulators (secondary batteries), which have a reversible discharging reaction.

In the 19th century, no difference was made between batteries and fuel cells. Today the definitions have been refined: batteries convert and store electrical energy and are thus a thermodynamically closed system; energy storage and conversion occur in the same compartment. Fuel cells are open systems in which the anode and cathode are just charge-transfer media and the active masses undergoing the redox reactions are delivered from outside the cell, either from the environment (for example, oxygen from air), or from a tank (for example, fuels such as hydrogen and hydrocarbons). Energy storage (in the tank) and energy conversion (in the fuel cell) are thus locally separated.

Not all systems can be described using this definition however, as there are also hybrids, such as metal–air batteries, which contain a battery electrode (metal anode) and a fuel-cell electrode (air cathode), or redox flow batteries, which are a form of rechargeable battery in which electrolyte containing one or more dissolved electroactive species flows through an electrochemical cell. Additional electrolyte is stored externally, generally in tanks, and is usually pumped through the cell of the reactor. The best-known example is the chromium–iron battery; Fe^{3+} and Cr^{2+} ions form the active masses. In these redox storage devices, the mechanical ageing of the accumulator electrodes is prevented. Flow batteries can be rapidly recharged by replacing the electrolyte whilst simultaneously recovering the spent material. Owing to the overlapping properties of batteries and fuel cells, it is nowadays considered appropriate to define the two systems together again, and thus no longer differentiate between batteries and fuel cells, as in former times.

A fuel cell is an electrochemical conversion device. It produces electricity from fuel on the anode side and an oxidant on the cathode side; these react in the presence of an electrolyte. Fuel cells can operate continuously as long as the necessary flows of reactants and reaction products are maintained; they are thus thermodynamically open systems. Many combinations of fuel and oxidant are possible. A hydrogen cell uses hydrogen as fuel and oxygen (usually from air) as oxidant. Other fuels include hydrocarbons and alcohols, and other oxidants include chlorine and chlorine dioxide.[7]

The principle of fuel cells has been known for over 165 years. In 1838, Christian Friedrich Schönbein discovered that an electrical voltage can be measured between two platinum wires, surrounded by hydrogen and oxygen, in an electrolyte solution. He published these results under the title "On the Voltaic Polarization of Certain Fluid and Solid Substances". Sir William Robert Grove investigated the new effect intensely and was the first to develop useable fuel cells. He connected several elements in series and called these systems "gas batteries". The further development of this concept to form a highly efficient electrical source proved to be so difficult that it took one hundred years until it improved significantly. After the design of the first electrical dynamo by Werner von Siemens in 1867, electrical generators were energy sources that efficiently delivered electricity in almost unlimited amounts. For this reason, fuel cells were almost completely superseded at the time.

Fuel cells can potentially convert chemical energy into electrical energy in a highly efficient manner; at the present time, the attainable efficiency is up to 65%, depending on the fuel and on conditions. Fuel cells can substitute other technologies or be operated together with, for example, combustion engines in co-generation of electricity and of heat and cold, and in residential or mobile applications. Figure 3 shows a comparison of the thermodynamic efficiencies of a hydrogen/oxygen fuel cell and of a Carnot cycle. In the future, fuel cells may be able to convert fuels into electrical energy with efficiencies of more than 70%. The difference between the theoretical and practical energy storage capabilities is related to several factors, including 1) inert parts of the system, such as conductive dilution agents, current collectors,

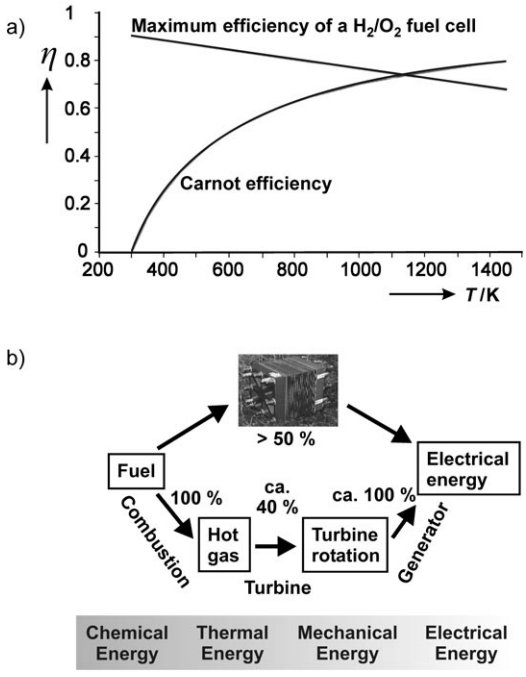

Figure 3. a) Ideal thermodynamic efficiency of polymer electrolyte membrane fuel cells (PEMFCs) in comparison with that obtained in the Carnot process. b) Comparison of processes in a co-generated heat engine with fuel-cell performance.

and containers, that are necessary for its operation, 2) internal resistances within the electrodes and electrolyte and between other cell/battery components, resulting in internal losses, and 3) limited utilization of the active masses, for example some of the fuel leaving the cell without reaction or passivation of electrodes, making them partially electrochemically inactive.

Fuel cells offer the cleanest power generation possible. They are quiet in operation and can be located close to the application, and they produce much less greenhouse emissions and can be more efficient in conversion of the energy in a fuel into power than gasoline engines or thermal power plants. Fuel cells are best utilized as a steady energy source and not as a power source to supply dynamic demands. For applications that require varying power demands, such as automotive propulsion, the use of the fuel cell in a hybrid configuration with a battery or an electrochemical capacitor is required. The fuel cell provides steady power demand whilst the battery or the electrochemical capacitor handles the surge for regenerative breaking and acceleration as well as initial start-up.

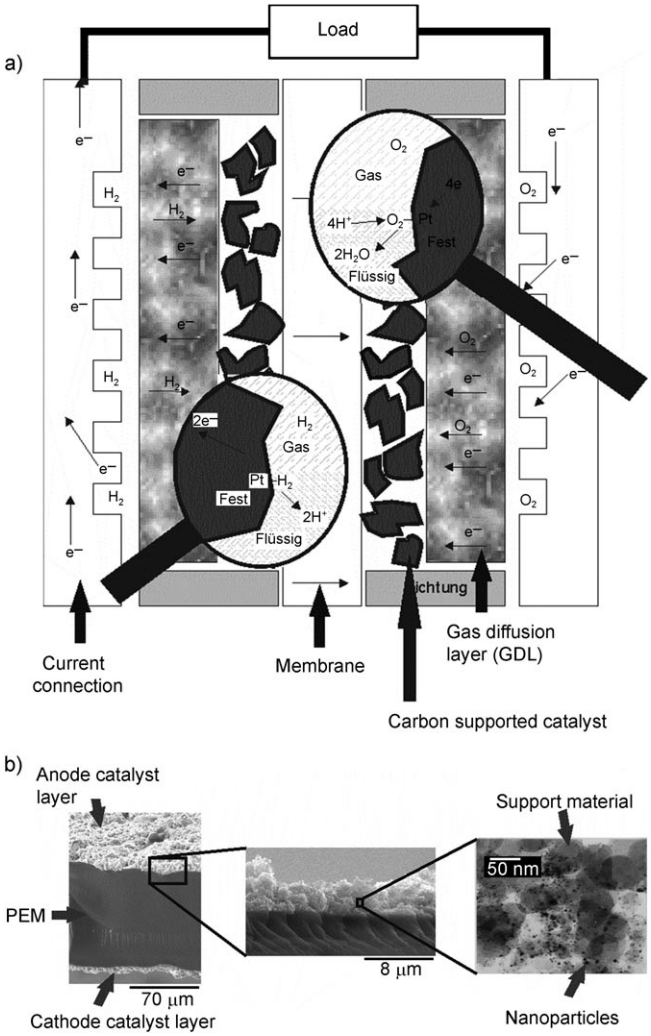

Figure 4. a) PEM fuel cell, with current connection, membrane (PEM), carbon-supported catalyst, and gas diffusion layer (GDL). b) Cross-section of a membrane electrode assembly (MEA), SEM image of a standard MEA, with platinum nanoparticles on Vulcan XC72, and a Nafion membrane as standard PEM.

There is a certain number of fuel cells that are currently under development; one important type is the polymer electrolyte membrane fuel cell (PEMFC; Figure 4). PEMFCs are being developed for stationary, portable, and mobile applications. Their distinguishing features are the membrane electrode assembly (MEA), which consists of a gas diffusion layer (carbon-fiber cloth), a special proton conducting membrane, typically Nafion, and an anode and cathode catalyst layer. In the heart of a fuel cell at low operation temperatures (50–120 °C), activated processes play a crucial role.

At high operation voltages, the power output of a fuel cell is controlled by the electrocatalytic properties of the catalyst. Challenges in fuel-cell catalyst research are to obtain high electric power density, high electric conversion efficiency, and low material costs. At high electric power density (more than 1 $W cm^{-2}$), high operation voltages are desirable; at high operation voltages (more than 0.8 V), the current density is controlled by the charge transfer, and the dissipated heat is minimized (Figure 5).[8]

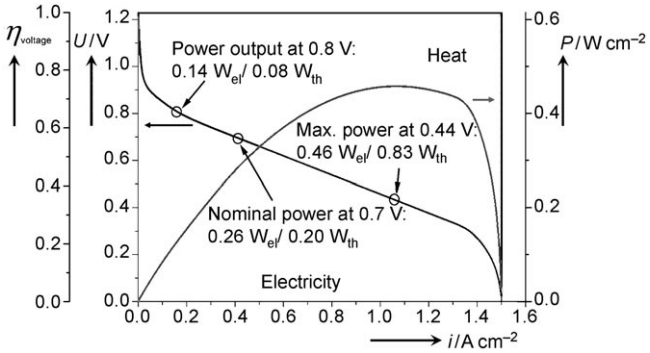

Figure 5. Conversion of chemical energy in fuel cells (voltage efficiency $\eta_{voltage}$ versus current density i). Black line: cell voltage U; gray line: power density P.

For high electric conversion efficiency, it would be desirable to use less co-generated heat, which would also allow for a simplification of the design and the need of less fuel (hydrogen) for the same electrical energy. To achieve low material costs, less noble metal should be incorporated, because high catalyst utilization is needed, and highly efficient catalysts are required for anode and cathode site. The goal in fuel-cell research must therefore be a deeper understanding of the parameters controlling electrocatalytic activity, which would enable us to propose rational structures for catalysts in fuel cells in the future.

High-temperature fuel cells, such as molten carbonate fuel cells (MCFCs) or solid oxide fuel cells (SOFCs), deliver heat at high temperatures ($T > 600$ °C). This heat can be used in high-temperature fuel-cell co-generation for district heating (heat extraction), for absorption refrigerators, and heat pumps. As the energy demand in residential applications for heating and for cooling over a year is complementary, such a combination would be very useful. The typical energy demand in residential applications is shown in Figure 6.[9]

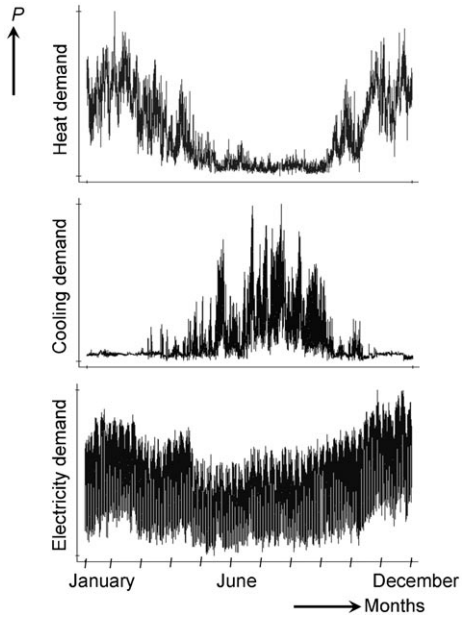

Figure 6. Typical heat, cooling, and electricity demand in residential applications over one year.

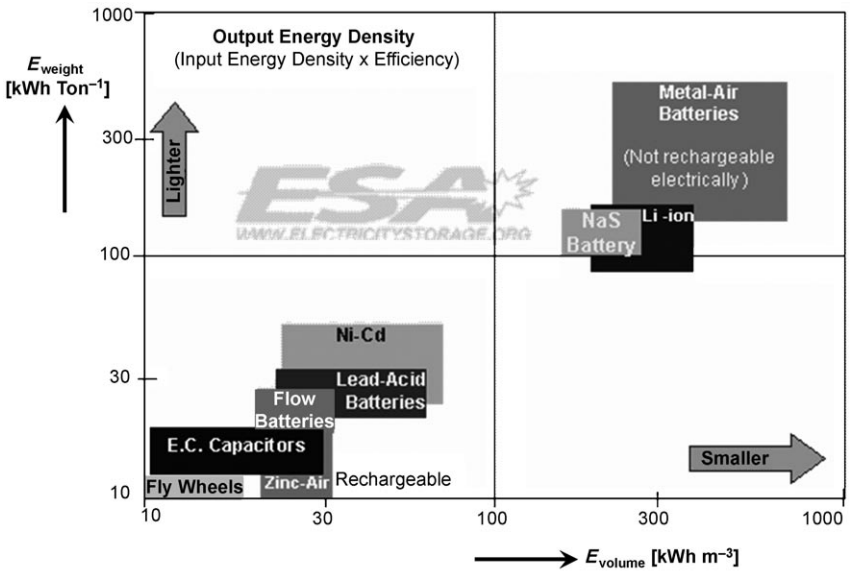

Figure 7. Overview of electrochemical energy storage devices.

Energy storage can be also performed by electrolysis, which can generate hydrogen (fuel) and oxygen. In electrolysis, chemical compounds are decomposed using electrical energy, which results in an increase in their chemical energy. Hydrogen can be generated electrochemically, for example by using PEMFCs based on platinum, or high-temperature alkaline electrolyzers based on nickel, with efficiencies of about 80%. Hydrogen might be the basis for a future hydrogen economy. The efficiency of hydrogen storage is low (less than 40%) compared to 60–70% achieved with a battery. An overview of electrochemical energy storage devices is given in Figure 7.[10]

In his article published in the *Zeitschrift für Elektrotechnik und Elektrochemie*,[5] Wilhelm Ostwald made the following statement: *"The persuasion is spread among large circles of technology that the scientific electrochemistry following its latest development, is qualified to help the technology exploring the new land and building its paths."*

3.2. Microscopic Aspects in Electrocatalysis

Another note of Wilhelm Ostwald describes the scientist as a predictor of prospective developments: *"When we ask for the general function of science, just as we do in the case of art, the answer is very straight forward: it consists of prophecies. All the manifold work driven by the sciences has the final goal to give us the potential to foresee future occurrences"*.[11] Even though, to some extent, his predictions were proven to be right, it is still not entirely understood which mechanism is responsible for an effective performance of an electrochemical energy conversion and storage device, like a fuel cell.

To gain more insight into the mechanisms that are taking place in a fuel cell, nanostructured electrodes are frequently employed as model catalysts to achieve a basic understanding of electrocatalytic properties. In particular, the influence of particle size and particle dispersion of noble metal catalysts and a possible influence of the support material can be studied in detail. A large variety of studies contribute to a better understanding of the parameters influencing the electrocatalytic properties of catalysts, which is important for their rational design.[12–32] Possible parameters are the interparticle distance, particle morphology, chemical composition, and influence of the support.

Commercially available catalysts are typically supported on carbon. Some TEM images of carbon-supported catalysts are shown in Figure 8.[33,34] These catalysts must be improved in the future using the knowledge gained in recent investigations on model systems.

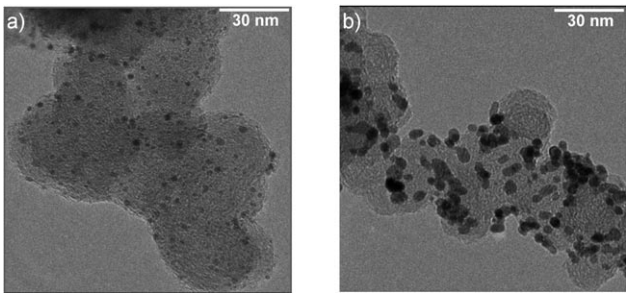

Figure 8. TEM micrographs of commercially available catalysts. a) Catalyst (E-TEK) with 10 wt% platinum on Vulcan XC72; b) Catalyst (E-TEK) with 40 wt% platinum on Vulcan XC72.

Results reported by Meier and Goodman[12] show that the binding energy of carbon monoxide and oxygen on small gold nanoparticles supported on TiO_2 is higher compared to larger gold particles. Using density functional theory (DFT) calculations, Janssens et al.[13] investigated gold particles, which show increased catalytic activity with decreasing particle size. This result was ascribed to low-coordinate gold atoms. Typically, carbon monoxide and oxygen do not adsorb on gold surfaces. Local reactivity measurements and combined DFT calculations of palladium nanoparticles on gold electrode surfaces were performed by Meier et al.[14,15] By investigating for the first time electrocatalytic properties of single nanoparticles, an increase of activity for the hydrogen evolution reaction by more than two orders of magnitude was found for a decrease of particle size from 200 nm to 6 nm. This result was explained by a strain effect in the palladium particles induced by the Au(111) substrate, which has a larger lattice constant. Investigations by Kibler[16] and Pandelov and Stimming[17] on monolayers and submonolayers of palladium on Au(111) electrode surfaces show that an enhanced catalytic activity is observed for the hydrogen evolution reaction with decreasing amount of palladium complementary to the results with palladium single particles.[14,15]

Selective variation of the catalyst substrate allows the influence of the support materials on the particle activity to be investigated. In the case of the hydrogen evolution reaction, experiments indicate that platinum nanoislands are more reactive on Au(111) than on highly oriented pyrolytic graphite (HOPG) substrates. In particular, a further increase in the reactivity for submonolayers indicates that the substrate is involved in the hydrogen evolution reaction. A possible explanation for this result is the spillover of adsorbed hydrogen from the nanoislands on gold.[35] Investigation of model systems with defined composition, such as bimetallic catalysts, helps to understand the role of the chemical composition of the catalyst material. Creating and investigating model surfaces with defined particle size will help to better understand the role of the size of catalyst particles. Investigating the interaction of particles as a function of particle dispersion will help to clarify the importance of the distance between particles on the support.

Electrocatalytic reactions, such as the hydrogen oxidation reaction (HOR), the hydrogen evolution reaction (HER), the oxygen reduction reaction (ORR), and the methanol oxidation reaction (MOR), are important for technical applications,[36] and are therefore studied in numerous investigations. Cyclovoltammetry on nanostructured surfaces, such as Pd/Au(111) and Pt/Au(111), showed that the specific activity of palladium and platinum on Au(111) for both HER and HOR increases with decreasing amount of palladium and platinum.[16,17,36] The activity of palladium and platinum on Au(111) for the ORR increases with increasing amounts of palladium; in this case, the specific activity is practically independent of the coverage.[36,37] The activity of platinum on Au(111) for the MOR increases with increasing amounts of platinum; increasing coverages lead to a decrease of the peak potentials to less positive values.

4. Summary and Outlook

The actual energy demand and consumption issues make it necessary to critically discuss and compare conventional thermodynamic volume processes and electrochemical interfacial processes. At present, only one third of the primary energy is converted into end energy, for example, electrical energy. Losses are associated with a high consumption of fossil fuel and large CO_2 emissions. These losses can be avoided by considering important electrochemical processes for energy conversion by using batteries and fuel cells, and by incorporating energy storage, employing rechargeable batteries, supercapacitors, generation of hydrogen by electrolysis, and generation of methanol.

Fuel cells offer the cleanest power generation possible, and could convert fuels into electrical energy with high efficiencies. Today, however, they cannot compete with heat engines because of much higher costs, inferior power performance, and insufficient durability and lifetime. As yet, no single electrochemical power source can match the characteristics of the internal combustion engine. A system that is competitive with heat engines can be envisioned when available electrochemical power systems are combined. In such hybrid electrochemical power systems, batteries and/or supercapacitors would provide high power and the fuel cells would deliver electricity with high efficiency. To achieve this aim, the costs of the electrochemical systems must however be reduced significantly.

Moreover, when we compare volumetric and interfacial systems, we face the genuine problem of geometry and thus the costs related to the space needed for both processes. This factor is one of the explanations of the long and constant success of heat engine systems compared to those based on electrochemistry. The fact that a coal power plant delivers power in the GW range and fuel cells in the MW range at most only shows that there is a general scaling problem. Possible strategies to overcome this problem could be decentralized power generation structures or the development of fuel cells with higher efficiencies. Even though these strategies are on their way to being successful, the advantages of conventional systems can still not be ignored.

Received: July 2, 2009
Published online: November 5, 2009

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