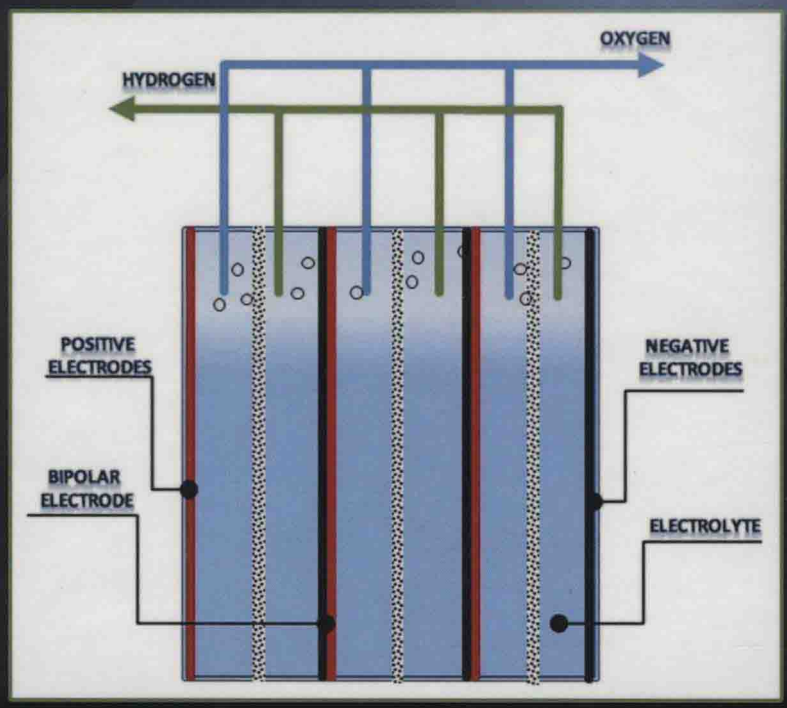
PEM Electrolysis for Hydrogen Production

Principles and Applications



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Nana Zhao

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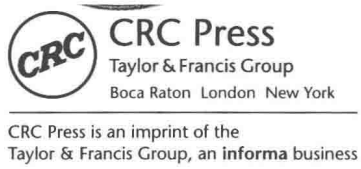

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Preface

Currently, there are two distinct commercial water electrolysis technologies that operate at low temperatures—alkaline and PEM (proton-exchange membranes) electrolyzers. Alkaline electrolyzers, a commercially more mature technology among the two, contain two electrodes immersed in a liquid alkaline electrolyte consisting of a concentrated KOH solution. In contrast, PEM electrolyzers use a solid proton-conducting polymer as the electrolyte and deionized water. As a result, PEM electrolyzers have many advantages over alkaline electrolyzers, such as a relatively simple system design and being able to operate safely at higher current densities. A third technology, currently at the precommercial stage, alkaline exchange membrane (AEM) systems, has the potential to place water electrolysis on a new cost reduction trajectory.

PEM water electrolysis has been known for many years; however, due to expensive components, such as membranes and bipolar plate materials and limited lifetime, PEM electrolyzers became established only in relatively small-scale niche applications, such as laboratory hydrogen and oxygen generators, life support systems, fuel supply for small fuel cell systems, etc. In general, PEM water electrolysis systems can provide a relatively simple, scalable, and easily deployable source of high-purity hydrogen for smaller retail and commercial applications near the point of consumption.

In recent years, hydrogen PEM fuel cells made significant progress toward commercialization, resulting in growing interest in technologies for hydrogen on-site production, such as PEM water electrolysis. Thus, the use of PEM water electrolysis for hydrogen fuel production became a vector of interest for fuel cell deployment opportunities in such sectors as sustainable mobility, material handling, and back-up power.

The rapid development of relatively small-scale PEM fuel cell technology also contributed to a "leapfrog" effect in the fundamental understanding of the requirements and functionalities of certain components and attributes of the PEM electrolysis technology that are both common for PEM fuel cells and electrolyzers, such as manufacturing aspects, components (membranes, plates, catalyst), flow-field design, etc. However, new trends in PEM water electrolysis systems development opened up new technology gaps and requirements that have not been discussed before with respect to PEM water electrolysis. For example, hydrogen is considered as one of the best solutions for large-scale energy storage that comes from renewable and intermittent power sources such as wind and solar electricity. If zero-carbon power sources, such as renewable or nuclear power, are used in combination with large-scale PEM water electrolysis, the resulting system will become suitable for large-scale clean and economically attractive hydrogen production and energy storage applications. Water electrolysis provides a sustainable solution for hydrogen production and is very well suited to be coupled with renewable energy sources. Thus, yet another vector of hydrogen applications for energy storage, called power-to-gas, is emerging and large utility companies are becoming involved.

To address technology gaps for large-scale PEM water electrolysis systems, the following areas require additional development: improved stack performance, scale up to megawatt size, grid integration, high pressure operation, high current density operation, degradation of components associated with transient operation, and a variety of market issues. All of these gaps relate directly to increased participation of PEM water electrolysis systems in hydrogen markets for various applications, not limited to fuel cells only. Megawatt scale-up, needed for such applications as power-to-gas and on-site refueling stations, includes requirements to reduce capital costs by 50% on a per kilowatt basis and availability of low-cost testing facilities; for example, electricity costs for PEM electrolysis megawatt testing can alone be a great challenge. Another challenge that the PEM water electrolysis industry has hardly discussed before is the large-scale manufacturing of cathode catalyst-coated membranes and stack components, availability of iridium, etc.

It is expected that demand for hydrogen as a fuel for fuel cells in both transport and stationary applications will continue to grow, alongside hydrogen for energy storage (the power-to-gas vector), thus generating more and more demands for PEM water electrolysis systems of large capacities.

It is well recognized that PEM water electrolysis systems are robust and dynamic. These systems can offer a fast response to volatile renewable energy sources. Due to the use of a dense proton-exchange membrane, PEM water electrolysis systems are capable of producing hydrogen at relatively high and practical discharge pressure, suitable, for example, for the injection of hydrogen into the grid of natural gas pipes. PEM water electrolyzers can also be scaled up to address various demands for energy storage.

Addressing climate change and the associated need for increasing renewable energy supply makes energy storage a critical technological component of the future

energy landscape. PEM water electrolysis when coupled with renewable energy sources and when electrolytic hydrogen is used to capture CO_2 to produce synthetic methane via the Sabatier reaction can also be attractive as an additional power-to-gas application reducing CO_2 emissions.

Due to the ever-increasing desire for green energy, the last decade has seen regained research interest in PEM electrolysis. However, significant challenges still remain for PEM electrolysis to be a commercially feasible large-scale hydrogen production solution. These challenges include the insufficient durability of the catalysts and membrane, high cost associated with the use of platinum group metal-based catalysts, corrosion of the current collectors and separator plates, and the development of a stack concept for the megawatt power range.

The intention of this book is to provide a comprehensive research source for PEM electrolysis, discuss fundamental aspects as well as examples of applications, provide a review of the state-of-the-art technologies and challenges related to each of the components of the PEM electrolysis, identify various failure modes and failure mechanisms, and discuss component degradation testing methods and protocols.

This book provides researchers and technology engineers with the most comprehensive and updated knowledge on PEM electrolysis technology, thus helping them identify technology gaps and develop new materials and novel designs that lead to commercially viable PEM electrolysis systems. We believe that students and professionals in disciplines such as electrochemical engineering, electrochemistry, material science in electrocatalyst development, material science in polymer development, and chemical and mechanical engineers working on energy storage and clean technologies will find this book useful.

Editors

Dr. Dmitri Bessarabov joined the DST HySA Infrastructure Center of Competence at North-West University (NWU) and Council for Scientific and Industrial Research (CSIR) in 2010. He is an internationally recognized scientist with academic and industrial decision-making experience in the area of hydrogen and electrocatalytic membrane systems for energy applications and fuel cells. Dr. Bessarabov has more than 15 years of progressively increasing responsibility in academic and industrial R&D environment and leadership roles in the hydrogen energy sector in Canada and South Africa. His current responsibilities include leadership in the National Hydrogen and Fuel Cell Program (HySA). He is currently also leading PEM electrolyzer development projects at the HySA Infrastructure, which includes the establishment of technology platforms for electrolyzer development, related characterization tools, electrochemical hydrogen compression, and hydrogen production using renewables.

Dr. Bessarabov received his fundamental training in chemistry at the renowned Lomonosov Moscow State University in Russia (MSc, 1991). He continued further education at the Russian Academy of Sciences in membrane gas separations at the Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences. In 1993, he joined the PhD program at the Institute for Polymer Science, University of Stellenbosch in South Africa. He earned his PhD in 1996, specializing in membrane technology for gas separation. His postdoctoral research at the University of Stellenbosch was in the area of electrocatalytic membrane systems and electrochemical ozone generation (1997–1998), for which NRF granted him a "Y" rating. In 1999, Dr. Bessarabov was appointed senior lecturer at the University of Stellenbosch's Chemistry Department. In 2001, he joined Aker Kvaerner Chemetics in Vancouver, Canada, to work in the area of membrane technology for the chloralkali industry. In 2006, he joined Ballard Power Systems in Canada (and afterwards AFCC, Automotive Fuel Cell Cooperation Corp.), where he was leading an R&D group on MEA integration and evaluation. His main areas of professional interest include fuel cells, PEM electrolysis, hydrogen energy, hydrogen storage, hydrogen infrastructure, membranes, separations, applied electrochemistry, applied polymer science, environmental technologies, and water treatment. To date, he has published more than 100 journal papers and 14 conference papers, and has been issued three patents.

Dr. Haijiang Wang is a senior research officer and project manager in the National Research Council of Canada (NRC). He has been with NRC for 10 years. His research covers PEM fuel cell, electrolyzer, metal-air battery, microbial fuel cell, and lithium-sulfur battery. Dr. Wang earned his PhD in electrochemistry from the University of Copenhagen, Denmark, in 1993. He then joined Dr. Vernon Parker's research group at Utah State University as a postdoctoral researcher to study electrochemically generated anion and cation radicals. In 1997, he began working with Natural Resources Canada as a research scientist to carry out research on fuel cell technology. In 1999, he joined Ballard Power Systems as a senior research scientist to continue his investigations. After spending five years with Ballard Power Systems, he joined NRC in 2004. He is currently adjunct professor at five universities, including the University of British Columbia and the University of Waterloo. Dr. Wang has 30 years' professional research experience in electrochemistry and fuel cell technology. To date, he has published more than 160 journal papers, three books, 10 book chapters, 40 industrial reports, and 30 conference papers or presentations and has been issued five patents.

Dr. Hui Li is a research officer and a master project lead under the energy storage program at the National Research Council of Canada—Energy, Mining and Environment Portfolio (NRC-EME, which used to be the Institute for Fuel Cell Innovation). Dr. Li earned her BS and MSc in chemical engineering from Tsinghu University in 1987 and 1990, respectively. After completing her MSc, she joined Kunming Metallurgical Institute as a research engineer for four years and then took a position as an associate professor at Sunwen University for eight years. In 2002, she started her PhD program in electrochemical engineering at the University of British Columbia (Canada). After earning her PhD in 2006, she carried out one term of postdoctoral research at the Clean Energy Research Centre (CERC) at the University of British Columbia with Professors Colin Oloman and David Wilkinson. Since joining NRC in 2007, Dr. Li has been working on PEM fuel cell contamination and durability, PEM electrolysis, and zinc-air batteries. Dr. Li has many years of research and development experience in theoretical and applied electrochemistry and in electrochemical engineering. Her research is based on PEM fuel cell contamination and durability testing, preparation and development of electrochemical catalysts with long-term stability, catalyst layer/cathode structure, and

catalyst layer characterization and electrochemical evaluation, failure diagnosis and mitigation for PEM fuel cells and electrolyzers, and air-cathodes for zinc-air battery. Dr. Li has coauthored more than 30 research papers published in refereed journals and coedited three books related to PEM fuel cells. Dr. Li has two granted patents and one technology licensed to the Mantra Energy Group.

Dr. Nana Zhao is a research scientist at Vancouver International Clean-Tech Research Institute Inc. (VICTRII), Burnaby, British Columbia, Canada. Her research interests include synthesis, evaluation and characterization of PFSA and hydrocarbon ionomer and membranes; MEA design and fabrication; characterization and electrochemical evaluation of catalyst layer; membrane and catalyst layer durability testing and diagnosis; synthesis and characterization of CO_2 separation membranes; preparation and characterization of subnanometer porous membrane for proton transportation and gas transport; and inorganic nanocrystals synthesis and application. Dr. Zhao received her BS in polymer chemistry and physics from Beijing Normal University in 2000. After that, she joined Changchun University of Science and Technology as a teaching assistant for two years and then started her PhD program on polymer chemistry and physics at Changchun Institute of Applied Chemistry, Chinese Academic Sciences, in 2002. After earning her PhD in 2008, she joined Professor Ting Xu's group as a postdoctoral fellow in material science and engineering at the University of California, Berkeley. At the same time, she also worked at Professor Frantisek Svec's team in Molecular Foundry at the Lawrence Berkeley National Laboratory. After one term of postdoctoral research, she took a position as a research associate at the National Research Council of Canada—Energy, Mining and Environment Portfolio (NRC-EME, which used to be the Institute for Fuel Cell Innovation) for two years. In 2013, she began working at VICTRII as a research scientist. Currently, she is taking a lead role in several collaborative PEM fuel cell projects.

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Overview of PEM Electrolysis for Hydrogen Production

Nicola Briguglio and Vincenzo Antonucci

CONTENTS

1.1 Introduction

The expression "hydrogen economy" is used to indicate the role of hydrogen in the future energy scenario. Interest in hydrogen, as an energy carrier, has been growing in the recent years due to heightening of air pollution in the world. Hydrogen is a clean and flexible energy carrier that can be used to provide both power and heat across all end-use sectors. Vehicles and stationary power generation fed by hydrogen are local zero emission technologies. Hydrogen can be produced from both traditional fossil fuel and carbon-free energy sources, which are used to store energy and to provide response management to electricity grid. Today, only 4% of hydrogen is produced from electrolysis; other lower-cost methods are preferred, such as steam reforming of natural gas or refinery gas. However, in the next future, the renewable energy sources (RES) will take up an important portion of electric energy produced. In this context, the energy storage is expected to play a key role in the future as "Smart Grid." The future energy storage technologies should be more flexible and able to balance the grid, ensuring stability and security. Large-scale deployment of variable renewable source (primary wind and solar energy) will be required to store energy to avoid the RES curtailment. Electrolysis is considered as the cleanest way to produce hydrogen using RES and has (along with other storage technologies) the potential as "energy storage" in this sector. In particular, bulk energy storage technologies are expected to have a key role for the integration of large amount of electricity produced from RES. This sector is dominated by pumped hydro as energy storage (PHES) in the world due to its large unit sizes and history. Anyway, long construction times and high uncertainty of future electricity price developments make PHES systems risky investments. Furthermore, constructions of PHES systems are strongly dependent on certain geographic requirements and topographical conditions.

Other technologies are compressed air energy storage (CAES), thermal energy storage, batteries, and flywheels. Anyway, the selection of technology depends on key parameters such as energy capacity and discharge time.

An interesting emerging application of electrolyzers is in the sector "Power to Gas." The hydrogen produced by electrolyzers, connected to RES, is injected in the gas network. This approach permits to use gas pipelines as large "storage tanks" avoiding construction of new infrastructures. The amount of hydrogen injected depends on the countries' regulations. This problem can be overcome through methanation, in which hydrogen and carbon monoxide/dioxide are converted in sustainable methane. The hydrogen stored in the gas infrastructure could be used for heating, in transportation, or reconverted in electricity.

Refueling stations with on-site hydrogen production are another application for electrolyzers. However, other technologies could be more cost-effective (i.e., steam methane reforming) than electrolysis. The choice of using electrolyzers will depend on local strategies, electricity price, etc. Uses of electrolyzers are not easily predictable in this sector.

Literature, conferences, and industry stakeholders on the energy sectors show that some issues must be resolved before electrolysis can be a competitive alternative, such as capital costs, lifetime, and system integration with energy services. Electrolyzers employed to store energy produced by intermittent RES need to operate dynamically with a lot of starts/stops. Pilot demonstration projects around the world on electrolyzers connected to RES are in progress, but the effects of these conditions on the stack and system durability have yet to be explored in depth. In fact, electrolyzers are usually designed to operate at constant conditions for industrial applications (i.e., chemical and food industry).

A recent study commissioned by the FCHJU (FCH JU report 2014) showed that electricity represents 70%–90% of the cost of a kilogram of hydrogen produced from electrolysis. As a consequence, the competitiveness of electrolysis will strictly relate to electricity prices. However, electrolysis can compete in circumstances where regulations permit a payment for grid services by operating as a controllable load or where policy context creates conditions to significantly reduce the cost of electricity.

1.2 Hydrogen Production

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy, as in the following equation:

$$H_2O + \text{electricity} \rightarrow H_2 + \frac{1}{2}O_2 \qquad (1.1)$$

Among the electrolysis technologies, alkaline electrolysis is at a mature stage, but some improvements as current density and working pressure can be made.

PEM electrolysis is in a precommercial phase in small-scale application. The research is mainly addressed toward the cost reductions of stack components and catalysts, and integration with RES.

Solid oxide electrolysis (SOE) is a technology under development and is not yet commercialized, but its technical advantages include potentially higher efficiency than other electrolysis technologies. SOE has also been used to produce CO from CO_2 and syngas H_2/CO from H_2O/CO_2.

Another interesting technology is the anion exchange membrane (AEM) electrolysis. This technology is in an early stage of development. The main advantage is the lower cost of catalysts than traditional PEM electrolysis, whereas the drawback is the low ion conductivity of membrane.

1.2.1 Solid Oxide Electrolysis

In an SOE, electricity is provided to electrochemically convert steam or CO_2 into hydrogen and CO. In the 1980s, this technology received great interest due to a study carried out by Donitz and Erdle, where a tubular SOE was demonstrated within the HotElly project. Following this, Westinghouse developed a tubular electrolysis based on the design used for SOFC. Interest in energy storage through hydrogen has led to new research activities on SOE in the last decade (Figure 1.1).

Examples of this renewed interest are the European project "Relhy" (http://www.relhy.eu/), which focuses on the development of low-cost materials and new components for SOE, and the research activities performed by universities in France, Germany, Denmark, and Japan.

The scheme of solid oxide electrolysis is shown in Figure 1.2.

Water is fed to cathode and oxygen ions are transported to the anode side through the electrolyte, and hydrogen is produced at the cathode side. If the cathode is also fed with CO_2, the overall electrochemical reactions of electrolysis are as follows:

$$\begin{cases} H_2O + 2e^- \rightarrow H_2(g) + O^{2-} \\ CO_2 + 2e^- \rightarrow CO + O^{2-} \end{cases} \quad \text{(cathode)} \qquad (1.2)$$

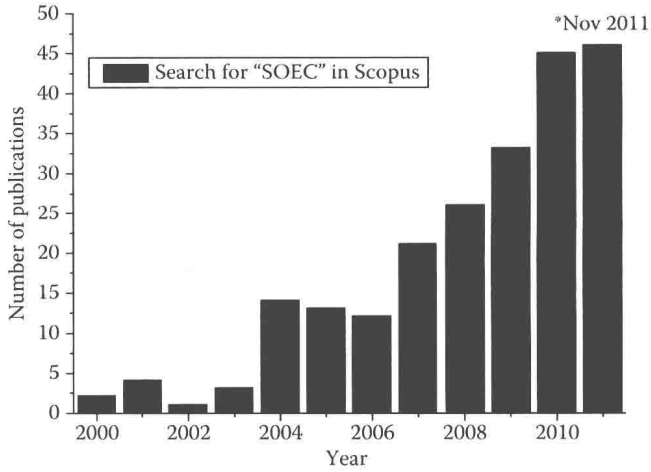

FIGURE 1.1
Number of publications per year in SOEC according to Scopus database. (Reprinted from *Journal of Power Sources*, 203, Laguna-Bercero, M.A., Recent advances in high temperature electrolysis using solid oxide fuel cells: A review, 4–16, Copyright [2012], with permission from Elsevier.)

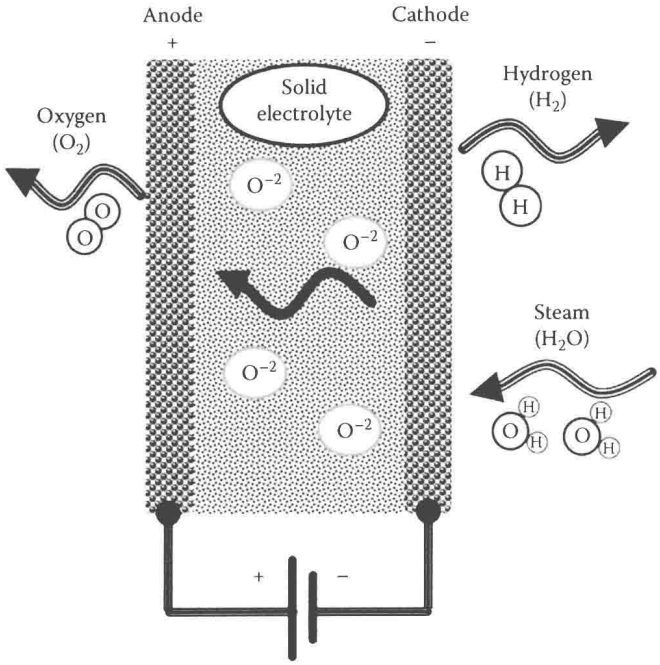

FIGURE 1.2
Sketch of an SOEC.

$$2O^{2-} \rightarrow O_2(g) + 4e^- \quad \text{(anode)} \tag{1.3}$$

Materials and technology used in SOE are based on that of solid oxide fuel cells (Laguna-Bercero 2012). The most common electrolyte material is YSZ (yttria-stabilized zirconia). This material shows high ionic conductivity, chemical, and thermal stability at working temperature (800–1000°C). Other potential candidates are ScSZ (scandia-stabilized zirconia), LSGM (lanthanum, strontium, gallium, manganite), and GDC (gadolinium-doped ceria) (Moyer et al. 2010). Materials for cathode include porous cermet of YSZ and metallic nickel (Ni–YSZ), samarium-doped ceria (SDC), titania/ceria composites, and various LSCM (lanthanum, strontium, chromium, manganite)-doped perovskites.

For anode, the most common material is the LSM (lanthanum, strontium, manganite), but other materials have also been proposed such as LSF (lanthanum, strontium, ferrite) or LSCo (lanthanum, strontium, cobaltite).

High temperature permits to reduce the electrical power demand as electrolysis process is increasingly endothermic with increasing temperature (Figure 1.3). The step of enthalpy curve at 100°C is due to the evaporation heat of water. After 100°C, the total energy demand remains quite constant, whereas the electric energy decreases and the heat demand increases. As a consequence, SOE could considerably reduce the cost of hydrogen if heat is supplied by waste heat.

The current research activities are focused on development of new materials stable at high temperature.

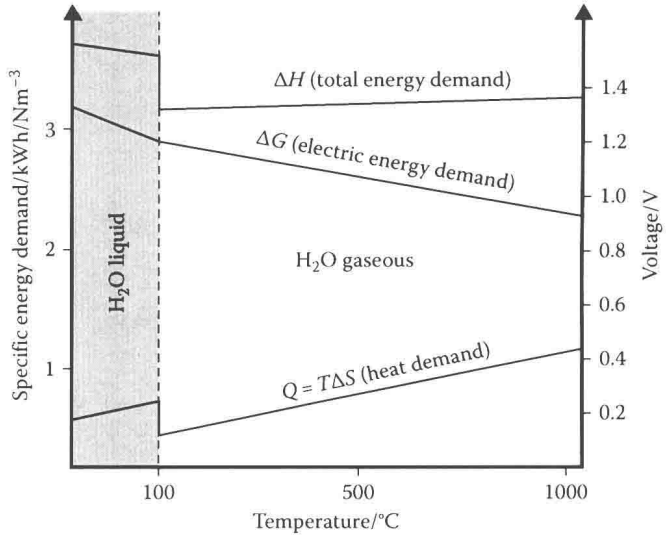

FIGURE 1.3
Electrolysis energy demand.

Today, the commercial products of SOE are not available, but the technology has been proven at laboratory scale.

1.2.2 Alkaline Water Electrolysis

Alkaline electrolyzers use an aqueous caustic solution of 20%–30% KOH as electrolyte. Today, it is the most mature technology up to megawatt range at commercial level. A description of process is shown in Figure 1.4. The cell is composed of two electrodes separated by a diaphragm used to avoid the recombination of hydrogen and oxygen produced. The diaphragm should have

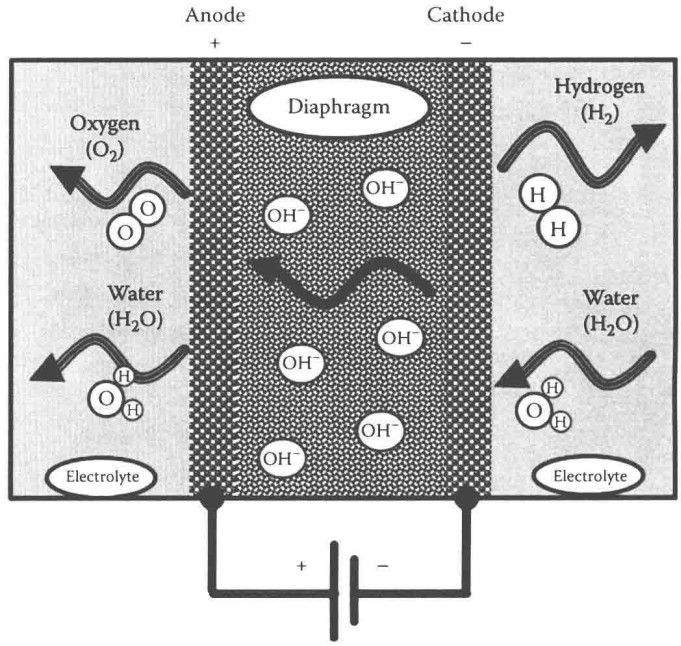

FIGURE 1.4
Alkaline electrolysis process description.

high chemical and physical stability with a high ionic conductivity. Typical operation temperature range is from 65°C to 100°C.

The basic reactions that take place in alkaline electrolysis are reported in Equations 1.4 and 1.5.

$$2OH^- \rightarrow \frac{1}{2}O_2(g) + H_2O + 2e^- \quad \text{(anode)} \qquad (1.4)$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad \text{(cathode)} \qquad (1.5)$$

Hydrogen and oxygen gas bubbles, produced at cathode and anode, respectively, increase the cell resistance reducing the contact between the electrodes and electrolyte. As a consequence, efficiency is reduced. Particular attention should be given to cell design to maximize the contact between the electrode and the liquid electrolyte. Advanced alkaline cell uses a "zero gap configuration" to reduce the impact of gas bubbles and the ohmic losses by reducing the space between the electrodes (FCH JU report 2014; Ursú et al. 2012).

The main drawbacks related to alkaline technology are the corrosive environment, the low current density, and the limited production rate of 25%–100% due to the diffusion of gases through the diaphragm at partial load. Typical operative pressure of this technology is 25–30 bar, but electrolyzers up to 60 bar are available.

Concerning the stack cost breakdown, the alkaline technology shows that the components have the main contribution in terms of size and weight due to low current density, refer Figure 1.5 (FCH JU report 2014). However, the cost of stack strictly depends on manufacturers.

There are two cell structures of alkaline electrolysis on market, unipolar and bipolar as reported in Figure 1.6.

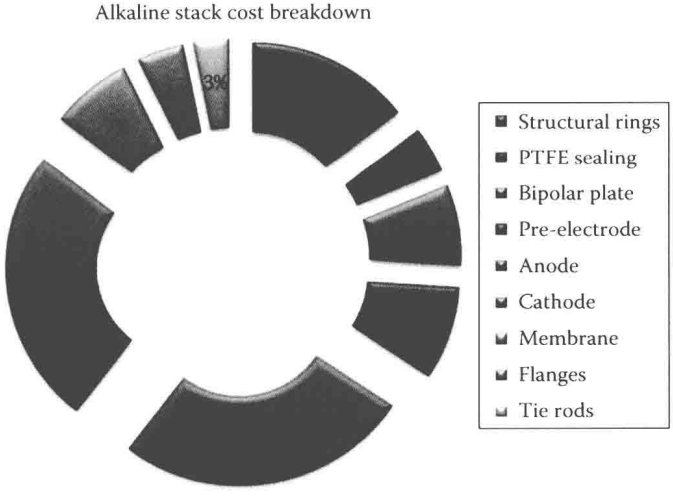

FIGURE 1.5
Stack cost breakdown for alkaline technology. (Modified from FCH JU report 2014, Study on development of water electrolysis in the EU 2014.)

In the monopolar configuration, the cells are connected in parallel and the electrodes are connected to the corresponding DC power supply. The total voltage applied to the stack is the same of that applied to an individual cell, and the electrodes have a single polarity.

Monopolar configuration is simpler from a fabrication point of view and permits a more easy maintenance and reparation without shutting down of the whole stack. Anyway, the disadvantage is that it usually operates at lower current densities and lower temperatures.

In the bipolar configuration, each electrode has two polarities and the cells are connected in series. The voltage applied to the stack is the sum of single-cell voltage. The current that flows through the stack is the same for cells.

The advantages of the bipolar design are higher current densities, which have capacity to produce higher pressure gas, and a more compact stack than unipolar design. The disadvantage is that it cannot be repaired without servicing the entire stack.

1.2.3 PEM Water Electrolysis

PEM water electrolyzers use a polymer electrolyte membrane (or proton exchange membrane) as ionic conductor. The scheme of operation of a PEM water electrolyzer is shown in Figure 1.7. Water is oxidized at the anode according to Equation 1.6 to produce oxygen and hydrogen evolves at the cathode according to Equation 1.7.

$$H_2(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+ + 2e^- \quad \text{(anode)} \qquad (1.6)$$

$$2H^+ + 2e^- \rightarrow H_2(g) \quad \text{(cathode)} \qquad (1.7)$$

The electrolyte consists of a thin, solid ion-conducting membrane instead of the aqueous solution used in the alkaline electrolyzers. The membrane transfers the H^+ ion (i.e., proton) from the anode to the cathode side and separates the hydrogen and oxygen gases. The most commonly used membrane material is Nafion® from DuPont.

The main advantages of PEM electrolysis over the alkaline are related to greater safety and reliability because no caustic electrolyte is used. Besides, the possibility to operating at high differential pressure across the membrane avoids the oxygen compression. PEM electrolysis has faster ion transportation than alkaline due to the solid and thin membrane. In fact, liquid electrolyte has more inertia in transportation of ions (Rajeshwar et al. 2008). This aspect is particularly important when an electrolyzer operates under fluctuating conditions. Alkaline electrolyzer suffers from delayed reaction and difficulty in starting the system after shutdown. Besides, this technology can operate at higher current density (2 A cm^{-2} at 2.1 V and 90°C [Millet et al. 2011]) than alkaline electrolyzers.

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