



## Power-to-Methane: A state-of-the-art review

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### ARTICLE INFO

#### Keywords:

CO<sub>2</sub> recycling  
 Demonstration plants  
 Methanation  
 Power-to-Methane  
 Water electrolysis

### ABSTRACT

Power-to-Methane is a concept that converts electrical into chemical energy using CO<sub>2</sub> and H<sub>2</sub>O. The concept brings the possibility of connecting the power grid to different sectors, where CH<sub>4</sub> is needed such as mobility and industry. In this review, a comprehensive overview of the state-of-the-art of Power-to-Methane is presented. The Power-to-Methane process chain is described in detail. Fundamentals of water electrolysis are highlighted and cell technologies are discussed and assessed. CO<sub>2</sub> sources are pointed out, CO<sub>2</sub> separation technologies are depicted and compared, and some separation projects worldwide are listed. Thermodynamics of methanation process is analyzed; catalysts and reactors used are described and evaluated. Finally, Power-to-Methane plants in operation and construction are addressed.

### 1. Introduction

The power capacity from renewable energy sources has seen a rapid growth. In the last 10 years, the average annual growth amounted to 15.9% [1], whereby the variable renewable energy sources (VRESs; mainly wind and solar) have afforded the largest shares. These tendencies are expected to continue in the future [2].

Power produced from VRESs cannot match electrical demand to 100%. With the growth in investments in VRESs, solutions to reduce the inherent issue of VRESs become increasingly necessary [3–7]. The attractive option will remain the energy storage [8–18].

There are different energy storage technologies that can be classified according to their work principles: (i) electrical (superconducting magnetic energy storage), (ii) mechanical (pumped storage, compressed air, flywheels), (iii) thermal (latent heat, sensible heat, thermochemical), and (iv) chemical (supercapacitors, batteries, power-to-gas, power-to-liquid) [19–22]. Besides the work principles, the storage technologies differ in further characteristics such as energy capacity, response time, self-discharge, efficiency and operating constraints, covering different fields of applications [23]. Accordingly, an energy storage mix will be needed.

In regions, where a natural gas infrastructure exists, the Power-to-Methane (PtM) concept is a promising option to absorb and exploit surplus renewable energy [20]. Fig. 1 shows the principle of the PtM concept and applications for it. A PtM plant basically consists of a water electrolyzer, a CO<sub>2</sub> separation unit, if CO<sub>2</sub> is not available as pure gas or

in suitable gas mixture, and a methanation module [24–26]. At times of surplus power, H<sub>2</sub> is produced by water splitting in the electrolyzer. The generated H<sub>2</sub> and CO<sub>2</sub> are then converted in the methanation unit to a gas mixture that mainly contains CH<sub>4</sub> and H<sub>2</sub>O [27]. The product gas is then treated to a methane-rich gas, so-called synthetic natural gas (SNG) [28,29]. The SNG conditioning unit and balance-of-plant components are not depicted in the figure. The SNG produced can be used as fuel for mobility, in the residential sector, for power generation at times, when the power demand overbalances the power supply, and as raw material in industry.

The purpose of this review paper is to present an extensive updated state-of-the-art of PtM technology giving the reader a structured technical understanding of the technology. The paper is structured as follows. Water electrolysis is handled in Section 2. CO<sub>2</sub> for PtM is discussed in Section 3. Methanation is approached in Section 4. PtM plants in operation and construction are addressed in Section 5. Finally, conclusions are drawn in Section 6.

### 2. Water electrolysis

The conversion of electrical into chemical energy in form of H<sub>2</sub>, water electrolysis, is the first part of the PtM process chain. Fig. 2 illustrates a typical scheme of water electrolysis systems. A system mainly consists of an electrolysis stack, an ion exchanger to obtain a high purity of the water fed into the stack, H<sub>2</sub> and O<sub>2</sub> separators, and a converter for power conditioning [30]. A stack contains a number of cells

Abbreviations: AEL, alkaline electrolysis; GHSV, gas hourly space velocity; PEMEL, polymer electrolyte membrane electrolysis; PtM, Power-to-Methane; SOEL, solid oxide electrolysis; VRES, variable renewable energy source

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<http://dx.doi.org/10.1016/j.rser.2017.08.004>

Received 30 December 2016; Received in revised form 20 June 2017; Accepted 2 August 2017  
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**Nomenclature**

$E_T$	Thermal energy ( $J mol^{-1}$ )
$F$	Faraday's constant ( $C mol^{-1}$ )
$m_{H_2}$	Mass of hydrogen (g)
$M_{H_2}$	Molar mass of hydrogen ( $g mol^{-1}$ )
$Q$	Electric charge (C)
$T_K$	Absolute temperature (K)
$V$	Voltage (V)
$V_{Oh}$	Ohmic voltage (V)

$V_{OV}$	Overvoltage (V)
$V_r$	Reversible cell voltage (V)
$V_{act}$	Real cell voltage (V)
$V_{tn}$	Thermoneutral cell voltage (V)
$z$	Electric charge (dimensionless)
$\Delta G_R$	Gibbs energy ( $J mol^{-1}$ )
$\Delta H_R$	Reaction enthalpy ( $J mol^{-1}$ )
$\Delta S_R$	Reaction entropy ( $J mol^{-1} K^{-1}$ )

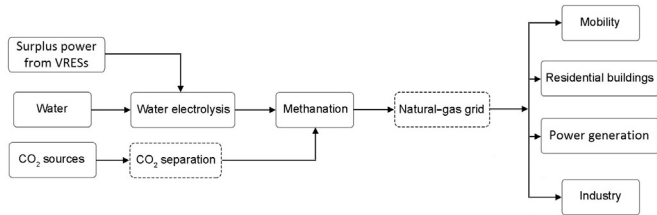


Fig. 1. Principle of the PtM concept and its applications.

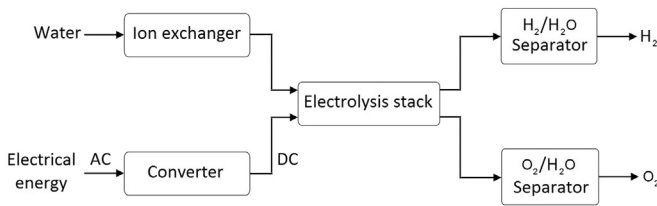


Fig. 2. Typical scheme of water electrolysis systems.

connected in series due to the low cell voltage. Each cell in turn consists of a cathode, an anode and an electrolyte in between. In general, three cell technologies named after their electrolytes can be distinguished: alkaline (AEL), polymer electrolyte membrane (PEMEL) and solid oxide (SOEL) [31]. The first two types are classified as low temperature electrolysis technologies since their typical operational temperature is lower than 100 °C [32]. The third one is classified as high temperature electrolysis that is operated at temperatures up to 1000 °C. In this section, fundamentals of the water electrolysis are first illustrated. The three electrolysis technologies are then presented and compared.

2.1. Fundamentals

The reaction equation of the water electrolysis process can be written as follows:



According to the Faraday's law of electrolysis [33], the relationship between the mass of hydrogen ( $m_{H_2}$ ) generated at a cathode and the electric charge ( $Q$ ) passed through the cathode is as follows:

$$m_{H_2} = \frac{M_{H_2}Q}{zF} \tag{2}$$

where  $M_{H_2}$  is the molar mass of hydrogen,  $z$  the number of electrons involved in the electrochemical reaction (Eq. (1)), and  $F$  the Faraday's constant [34].

The cell voltage required to decompose water (thermoneutral cell voltage ( $V_{tn}$ )) is proportional to the water decomposition enthalpy ( $\Delta H_R$ ):

$$V_{tn} = \frac{\Delta H_R}{zF} \tag{3}$$

According to the second law of thermodynamics and because the entropy change of the water electrolysis is positive [35], a part of the reaction enthalpy can be applied as thermal energy, which is the product of the entropy change of the water decomposition reaction ( $\Delta S_R$ ) and the absolute temperature ( $T_K$ ):

$$E_T = T_K \Delta S_R \tag{4}$$

The difference between  $\Delta H_R$  and  $T\Delta S_R$  is the change in the Gibbs energy of the water decomposition reaction ( $\Delta G_R$ ). This is proportional to the minimum cell voltage (reversible cell voltage ( $V_r$ )) needed to split  $H_2O$  [36,37]:

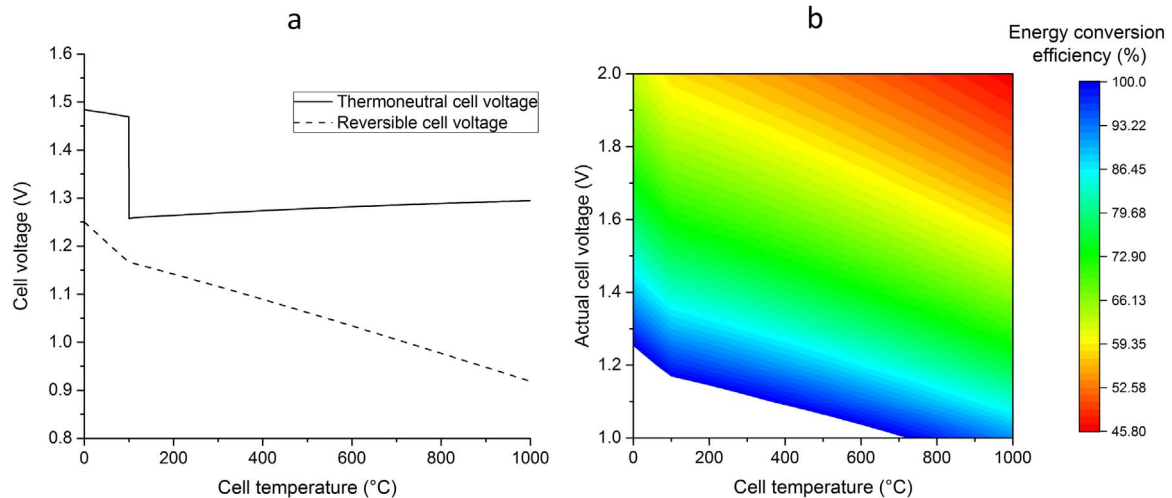


Fig. 3. a: thermoneutral and reversible cell voltages for water electrolysis as functions of temperature at 1 atm; b: energy conversion efficiency of water electrolysis as function of temperature and actual operating cell voltage at 1 atm.

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