Chinese Journal of Catalysis 39 (2018) 390–394

available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/chnjc

Review (Special Issue of Photocatalysis for Solar Fuels)

Water electrolysis based on renewable energy for hydrogen production

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ARTICLE INFO

Article history:
Received 7 October 2017
Accepted 26 October 2017
Published 5 March 2018

Keywords:
Water electrolysis
Hydrogen production
Renewable energy
Abandoned solar power
Abandoned wind power

ABSTRACT

As an energy storage medium, hydrogen has drawn the attention of research institutions and industry over the past decade, motivated in part by developments in renewable energy, which have led to unused surplus wind and photovoltaic power. Hydrogen production from water electrolysis is a good option to make full use of the surplus renewable energy. Among various technologies for producing hydrogen, water electrolysis using electricity from renewable power sources shows great promise. To investigate the prospects of water electrolysis for hydrogen production, this review compares different water electrolysis processes, i.e., alkaline water electrolysis, proton exchange membrane water electrolysis, solid oxide water electrolysis, and alkaline anion exchange membrane water electrolysis. The ion transfer mechanisms, operating characteristics, energy consumption, and industrial products of different water electrolysis apparatus are introduced in this review. Prospects for new water electrolysis technologies are discussed.

1. Introduction

As global warming and related environmental issues become more serious the development of renewable energy sources has become more important. Renewable energy sources, such as wind and solar power, have transient characteristics, which require proper energy management and storage. From data reported by the National Energy Administration, the surplus unused wind power in China accounted for 497×10^8 kWh in 2016, and unused solar power in the northwest totaled more than 7×10^6 kWh; the total photovoltaic (PV) power output was 28.7 billion kWh, which means that approximately 20% of photovoltaic power was unused [1]. The installed photovoltaic capacity in the northwest area of China, i.e., Xinjiang, Gansu, Qinghai and Ningsia, is greater than 5 000 000 kW. The distributed photovoltaic capacity in the middle east of China (i.e., Jiangsu, Zhejiang, Shandong, and Anhui) is greater than 1×10^6 kW. In some areas (i.e., Xinjiang and Gansu) the unused photovoltaic energy respectively accounts for 32.23% and 30.45% of the total energy produced, as reported by the National Energy Administration [2]. Hydrogen is a more suitable energy storage medium than other fuels, owing to the high heat value of hydrogen. The energy density of hydrogen is 140 MJ/kg, which is more than twice as high as that of typical solid fuels (50 MJ/kg). Hydrogen burns to produce water, making hydrogen an environmental friendly energy store. In terms of hydrogen storage, gaseous and liquid hydrogen can be stored in pressurized tanks, or in the solid state as

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This work was supported by the Joint Fund of National Natural Science Foundation of China (U1664259), the National Natural Science Foundation of China (91434106), the State Grid Fund (SGTYHT/15-JS-193) and the Beijing municipal science and technology commission project (Z171100002017024).
DOI: 10.1016/S1872-2067(17)62949-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

metal hydrides. Therefore, the advantages of hydrogen as an energy carrier are not only its high energy density, but also that hydrogen and electricity can be interconverted through water electrolysis. Furthermore, hydrogen could be used in a grid when hydrogen production is scaled-up.

There are several technologies available for hydrogen production, including reforming, decomposition, and hydrolysis of fossil fuels. Approximately four billion tons of hydrogen are required annually, with 95% of hydrogen production derived from fossil fuel, which also produces CO_2. Water electrolysis powered by renewable energy sources, is expected to enable the scale-up of hydrogen production, and zero CO_2 emissions are produced in water electrolysis processes. Typical characteristics of main electrolysis technologies are listed in Table 1. Hence, storing surplus solar and wind energy as hydrogen shows great promise. Hydrogen generated from water electrolysis has high purity (99.9%), and can also be used as a reactant for many industrial processes.

2. Water electrolysis for hydrogen production

In the water electrolysis process, water is the reactant, which is dissociated to hydrogen and oxygen under the influence of direct current.

Anode: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$

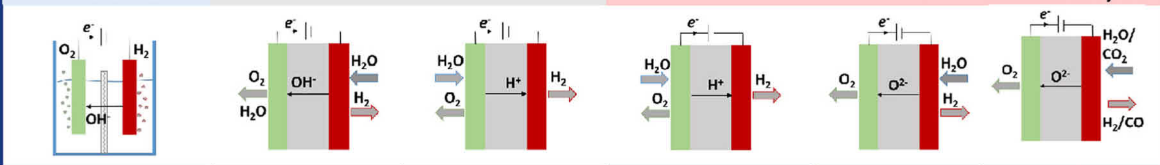
Overall: $H_2O \rightarrow H_2 + 1/2O_2$

Different electrolytes systems developed for water electrolysis include alkaline water electrolysis (AWE), proton exchange membranes (PEMs), alkaline anion exchange membranes (AEMs), and solid oxide water electrolysis (SOE). Different materials and operating conditions are used in these systems; however, the operating principles are the same. On the basis of different operating temperatures, low and high temperature water electrolysis are also possible.

2.1. Alkaline water electrolyzer for hydrogen production

Alkaline water electrolysis operates at low temperature (60–80 °C), with KOH and/or NaOH aqueous solution as the electrolyte, the concentration of the electrolyte is approximately 20%–30%. In an alkaline electrolyzer, the diaphragm is asbestos, and nickel materials are used as the electrode. The purity of the generated hydrogen is approximately 99%; however, an alkali fog in the generated gas must be removed, for which desorption is typically used. The maximum operating current density of an alkaline electrolyzer is less than 400 mA/cm^2, and the power consumption for H_2 production is approximately 4.5–5.5 kWh/Nm^3 with an efficiency of approximately 60%. To avoid hydrogen/oxygen penetrating the po-

Table 1
Typical characteristics of main electrolysis technologies. Reprinted with permission from Ref. [3], copyright 2017 Elsevier.

	Low Temperature Electrolysis			High Temperature Electrolysis		
	Alkaline (OH^-) electrolysis		Proton Exchange (H^+) electrolysis		Oxygen ion(O^{2-}) electrolysis	
	Liquid	Polymer Electrolyte Membrane		Solid Oxide Electrolysis (SOE)		
	Conventional	Solid alkaline	H^+ - PEM	H^+ - SOE	O^{2-} - SOE	Co-electrolysis
Operation principles						
Charge carrier	OH^-	OH^-	H^+	H^+	O^{2-}	O^{2-}
Temperature	20-80°C	20-200°C	20-200°C	500-1000°C	500-1000°C	750-900°C
Electrolyte	liquid	solid (polymeric)	solid (polymeric)	solid (ceramic)	solid (ceramic)	solid (ceramic)
Anodic Reaction (OER)	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$	$2H_2O \rightarrow 4H^+ + 4e^- + O_2$	$O^{2-} \rightarrow {}^1/_2O_2 + 2e^-$	$O^{2-} \rightarrow {}^1/_2O_2 + 2e^-$
Anodes	Ni > Co > Fe (oxides) Perovskites: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $LaCoO_3$	Ni-based	IrO_2, RuO_2, $Ir_xRu_{1-x}O_2$ Supports: TiO_2, ITO, TiC	Perovskites with protonic-electronic conductivity	$La_xSr_{1-x}MnO_3$ + Y-Stabilized ZrO_2 (LSM-YSZ)	$La_xSr_{1-x}MnO_3$ + Y-Stabilized ZrO_2 (LSM-YSZ)
Cathodic Reaction (HER)	$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$2H_2O + 4e^- \rightarrow 4OH^- + 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$4H^+ + 4e^- \rightarrow 2H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$ $CO_2 + 2e^- \rightarrow CO + O^{2-}$
Cathodes	Ni alloys	Ni, Ni-Fe, $NiFe_2O_4$	Pt/C MoS_2	Ni-cermets	Ni-YSZ Subst. $LaCrO_3$	Ni-YSZ perovskites
Efficiency	59-70%		65-82%	up to 100%	up to 100%	-
Applicability	commercial	laboratory scale	near-term commercialization	laboratory scale	demonstration	laboratory scale
Advantages	low capital cost, relatively stable, mature technology	combination of alkaline and H^+-PEM electrolysis	compact design, fast response/start-up, high-purity H_2	enhanced kinetics, thermodynamics: lower energy demands, low capital cost		+ direct production of syngas
Disadvantages	corrosive electrolyte, gas permeation, slow dynamics	low OH^- conductivity in polymeric membranes	high cost polymeric membranes; acidic: noble metals	mechanically unstable electrodes (cracking), safety issues: improper sealing		
Challenges	Improve durability/reliability; and Oxygen Evolution	Improve electrolyte	Reduce noble-metal utilization	microstructural changes in the electrodes: delamination, blocking of TPBs, passivation		C deposition, microstructural change electrodes