Journal of Membrane Science 514 (2016) 155–164

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Salinity gradient power-reverse electrodialysis and alkaline polymer electrolyte water electrolysis for hydrogen production

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ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form
9 April 2016
Accepted 29 April 2016
Available online 3 May 2016

Keywords:
Hydrogen production
Reverse electrodialysis
Salinity gradient power
Alkaline water electrolysis

ABSTRACT

In this work, innovative use of Salinity Gradient Power (SGP) as renewable energy source for indirect production of hydrogen is addressed. A lab-scale reverse electrodialysis (RED) unit, fed with different NaCl solutions mimicking highly concentrated brine (5 M), Reverse Osmosis retentate (1 M), seawater (0.5 M) and brackish water (0.1 M), was coupled to an alkaline polymer electrolyte (APE) water electrolysis cell. SGP-RED unit, equipped with 27 cell-pairs, reached at best an Open Circuit Voltage (OCV) of 3.7 V and maximum gross power density of 3.2 W m_{MP}^{-2} (membrane pair) when feeding the low concentration compartment (LCC) with 0.1 M NaCl and the High Concentration Compartment (HCC) with 5 M NaCl. The single-cell APE water electrolysis unit, operated at 1.8 V, attained a current density of 120 mA cm^{-2} under the following configuration: 10% w/w KOH electrolyte, highly conductive anion selective membrane composed of inert low-density polyethylene, finely milled anion selective particles and water-soluble poly (ethylene glycol-ran-propylene glycol), non-Platinum catalysts ($NiCo_2O_4$ and $NiFe_2O_4$) loading of 10 mg cm^{-2} and 15%w/w polymer binder at both cathode and anode, and operational temperature of 65 °C. The integrated system resulted in a maximum hydrogen production rate of 44 cm^3 h^{-1} per cm^2 of electrode surface area.

1. Introduction

With more than 50 million metric tons produced annually worldwide [1], hydrogen plays a strategic role in petroleum refining (i. e. hydrocracking, hydrodesulphurisation, hydroisomerization, dearomatisation), in ammonia production and in a range of applications of the electronics industry [2]; moreover, it is also recognized as a clean, efficient and versatile energy vector [3]. Large-scale H_2 generation has been so far dominated by fossil fuels: nearly 50% via steam reforming of natural gas, and about 46% from oil/naphtha reforming and coal gasification [4]. Water electrolysis, typically limited to small scale and so far representing only 4% of the world hydrogen production, is now receiving increased attention due to the possibility to use renewable power supply in the logic of a sustainable growth. Renewable energy resources such as photovoltaic and wind have been explored for electrolytic production of hydrogen from water [5]. However, use of solar and wind energy is limited by stability issues caused by intrinsic seasonal and weather-dependent character. Dutton et al. investigated the effects of power fluctuations on alkaline electrolyzers powered by wind turbines: although short-term variations do not have significant effects, intermittent operations protracted over several days resulted in pressure fluctuations with adverse effects on gas purity level [6]. In general, intermittent electrolysis operations may lead to damage and degradation of the separators

Abbreviations: AEM, Anion exchange membrane; APE, Alkaline polymer electrolyte; ASM, Anion selective membrane; BL, Binder loading; CC-GDL, Catalyst coated gas diffusion layer; CEM, Cation exchange membrane; CL, Catalyst loading; EIS, Electrochemical impedance spectroscopy; GDE, Gas diffusion electrode; HCC, High concentration compartment; HER, Hydrogen evolution reaction; HPR, Hydrogen production rate; IAR, Internal areal resistance; LCC, Low concentration compartment; MEA, Membrane electrode assembly; OCV, Open circuit voltage; PEM, Polymer electrolyte membrane; RED, Reverse electrodialysis; RO, Reverse osmosis; SGP, Salinity gradient power.

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http://dx.doi.org/10.1016/j.memsci.2016.04.067
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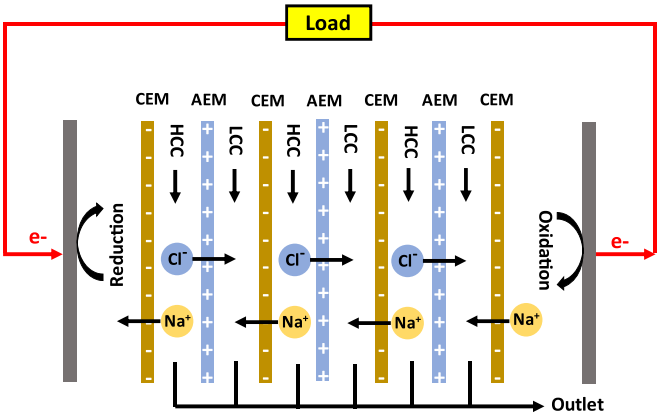

Fig. 1. The principle of energy production by SGP-*RED* stack. A voltage is continuously generated so long as the Low concentration compartment (LCC) and the High concentration compartment (HCC) are fed with NaCl solutions at different salinity.

due to local overload, deactivation of the electrode catalysts, corrosion caused by shortcut currents, gas crossover and pressure equalization between cathode and anode [7]. The capacity factor of intermittent renewable sources usually falls below 40% [8].

Salinity Gradient Power (SGP), the renewable energy extracted from mixing two solutions at different salinity, is recently attracting growing interest among the scientific community. Unexploited estuarial SGP, released when river and seawater mix together, has an estimated global potential of 2000 TWh yr^{-1}, which is more than 10% of the current world energy demand [9]. In principle, considering that energy requirement of electrolyzes falls in the range of 53–70 kWh kg^{-1} [10], an efficient utilization of the available SGP would produce up to 38 Mt yr^{-1} of hydrogen. One of the primary technologies capable to exploit SGP is Reverse electrodialysis (*RED*) [11–20].

A typical scheme of RED unit is illustrated in Fig. 1. Anion exchange membranes (AEM) and cation exchange membranes (CEM) are alternatively stacked between spacers to create adjacent low concentration and high concentration compartments (there after indicated as LCC and HCC, respectively). The chemical potential difference causes the transport of ions through ion exchange membranes from HCC to LCC solutions. Specifically, for NaCl solution, Na^+ ions tend to diffuse through CEMs towards the cathode, while Cl^- ions diffuse through AEMs in the opposite direction towards the anode; overall, a positive potential is generated on the left side of the stack. Transport of ions through the membranes occurs if an electrical load is connected to the electrodes placed at both sides of the membrane pile: the ionic current in the cells is converted into electron current at the electrodes by redox reactions. The electrical current and the potential difference over the electrodes can be used to generate electrical power [21].

The open circuit voltage (OCV) of the unit is given by the sum of Nernst potential raise over the cell pairs.

The potential generated by *RED* depends on the properties of the membranes, spacer material, geometry, number of cell pairs, operating conditions including salinity gradient level, temperature, flow velocity etc. For ideally permselective ion exchange membranes, the theoretical potential generated by a single cell pair is about .0.076 V for brackish water (0.1M)/seawater (0.5M), 0.13 V for seawater (0.5M)/brine (5M), 0.21 V for brackish water (0.1M)/brine (5M).

The thermodynamic threshold for water electrolysis is 1.23 V at 25 °C [22]. Among the currently available water splitting technologies, alkaline polymer electrolyte (APE) water electrolysis works in alkaline environment using non-precious metal catalysts [23,24]. A scheme of a typical APE water electrolysis unit for

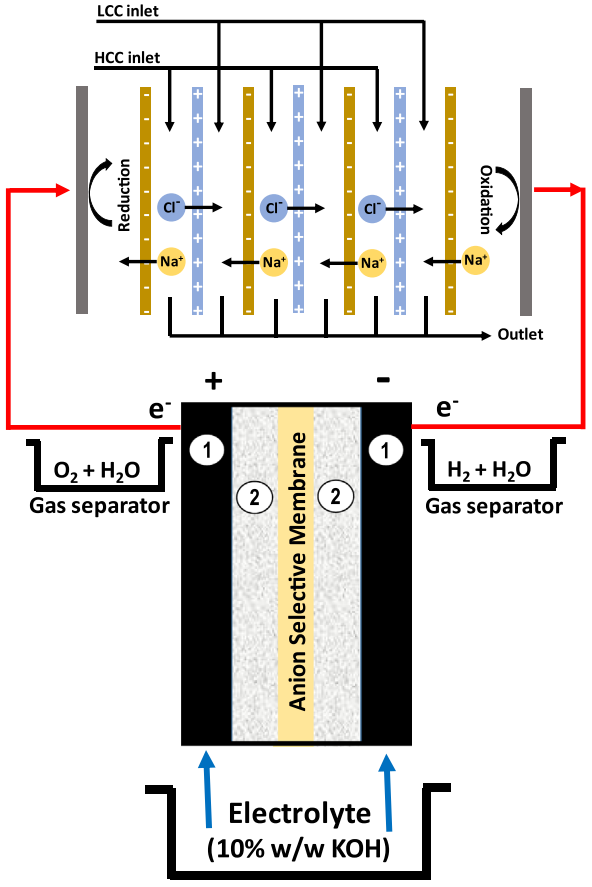

Fig. 2. Schematic illustration of alkaline electrolysis unit equipped with a solid polymer electrolyte (anion selective membrane): (1) gas diffusion layer; (2) catalyst layer.

hydrogen production consisting of a single cell equipped with a anion selective membrane (ASM) is reported in Fig. 2. When a direct current is applied to the electrodes, electrons flow from the anode to the cathode where hydrogen ions (protons) are reduced to gaseous hydrogen. Driven by the electrical field between the two electrodes, hydroxide ions are transferred through the AEM to the anode, and here are oxidized to O_2 returning electrons to the positive terminal. The half reactions occurring at the electrode surfaces of APE water electrolysis are:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (1)$$

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^- \quad (2)$$

resulting in the following overall reaction:

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \quad (3)$$

Few previous attempts in using *RED* for hydrogen production are reported in literature. In 2006, Seale patented a *RED* system for simultaneous generation of electricity and electrolytic production of hydrogen [25], followed by a patent of Logan et al. in 2014 [26]. Integration of reverse electrodialysis with microbial electrolysis cell (MEC) in a system called “microbial reverse-electrodialysis electrolysis cell (MREC)” was proposed by Logan et al. with the aim to produce hydrogen from renewable biomass [27–29]. Hatzell et al. investigated the use of thermolytic ammonium bicarbonate solutions for energy capture in a closed-loop *RED* system using either oxygen reduction or hydrogen evolution [30]. The