

Salinity Gradient Power Driven Water Electrolysis for Hydrogen Production

Ramato Ashu Tufa^{*a,b}, Debabrata Chanda^c, Lucrezia Tundis^a, Jaromír Hnát^b, Karel Bouzek^b, Joost Veerman^d, Enrica Fontananova^e, Gianluca Di Profio^e, Efrem Curcio^{a,e}

^aDepartment of Environmental and Chemical Engineering, University of Calabria, via P. Bucci CUBO 45A, 87036 Rende (CS) Italy

^bDepartment of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

^cSchool of Chemical Engineering and Advanced Materials, Newcastle University, Merz Court, Newcastle Upon Tyne, NE1 7RU, United Kingdom

^dREDstack BV, Pieter Zeemanstraat 6, 8606 JR Sneek, The Netherlands

^eInstitute on Membrane Technology of the National Research Council (ITM-CNR), c/o the University of Calabria, via P. Bucci, cubo 17/C, 87036 Rende (CS) Italy

ramatotufa@unical.it; tufaa@vscht.cz

The present work demonstrates an innovative system combining Reverse Electrodialysis (RED) and Alkaline Polymer Electrolyte Water Electrolysis (APEWE) for sustainable hydrogen production. The Salinity Gradient Power (SGP)-RED unit was tested with a thermally regenerative solution of NH_4HCO_3 in the concentration range of 0.15-1.5 M, whereas the water electrolysis unit equipped with quaternary ammonium functionalized anion selective membrane, Ni anode modified with Platinum Group Metal (PGM)-free electrocatalyst, Ni cathode modified with an electrochemically Reduced Graphene Oxide (RGO) was investigated at a varying temperature (50 - 80 °C). The integrated RED-APEWE system reached a maximum hydrogen production rate of 3.0×10^{-3} mol H_2/h per cm^2 of electrode surface area. Owing to the use of the thermally regenerative NH_4HCO_3 solution, this work presents a profound basis to design a system allowing the conversion of low-grade waste heat into electricity in a closed loop with simultaneous production of hydrogen using salinity gradient energy.

1. Introduction

The rapidly growing energy demand along with the extensive use of the limited fossil fuel and the consequent climate change issues drives the search for alternative energy sources with limited thermal and environmental pollution. Reverse Electrodialysis (RED) is emerging as a promising technology for conversion of salinity gradient energy into electricity. Research on RED so far has focused on membrane development, stack design and optimization, fouling and advanced applications in hybrid systems (Fontananova et al., 2017, Avci et al., 2016, Tufa et al., 2014, Tufa et al., 2016).

In RED, a series of Anion Exchange Membranes (AEM) and Cation Exchange Membranes (CEM) are alternatively stacked between two electrodes (anode and cathode), thereby creating adjacent low concentration compartments (LCCs) and high concentration compartments (HCC), which are fed by two aqueous salt solutions of different salinity. The salinity difference on either side of the membranes initiates selective transport of ions across ion exchange membranes towards the electrodes. The ionic current in the cells is converted into electricity by redox reactions at the electrodes.

Hydrogen presents a clean and versatile energy carrier that can address the issues of energy and environment (Chanda et al., 2014). Hydrogen can be produced by water electrolysis using renewable energies sources like wind and sun (Turchetti et al., 2015). However, such sources are associated with power fluctuations which might impact the electrolyzer performance (Dutton et al., 2000).

Alkaline water electrolysis is an industrially established, robust technology. The most significant development in alkaline water electrolysis is the use anion selective membranes (polymer electrolytes) attached to the electrodes, allowing a zero gap configuration. The advantages of such configuration are flexibility, reduced Ohmic losses and costs.

Recently, a non-intermittent SGP-RED has been demonstrated to be a viable alternative for sustainable hydrogen production. Tufa *et al.* (Tufa *et al.*, 2016) explored the potential of an Alkaline Polymer Electrolyte Water Electrolysis (APEWE) system powered by a RED generator for hydrogen production (Tufa *et al.*, 2016). The RED system equipped with 27 cells and total active membrane area of 0.27 m², integrally operated with APEWE system consisting of a highly conductive anion selective membrane, non-platinum catalysts (NiCo₂O₄) reached a maximum hydrogen production rate of 44 cm³/h per cm² of electrode area at 65 °C.

The use of thermolytic solutions such as ammonium bicarbonate (NH₄HCO₃) (AmB) opens up a new perspective in energy conversion, allowing power generation using low-grade waste heat in a closed loop. NH₄HCO₃ decomposes into a gaseous phase containing NH₃, CO₂ and water at temperatures above 40 °C, and it can be concentrated with low-grade waste heat (Cusick *et al.*, 2012). This allows subsequent regeneration of the salinity-gradient for RED stack.

The present work explores the potential of a novel RED-APEWE system for hydrogen production driven by SGP as a non-intermittent renewable energy source. The RED generator, functioning as power sources for APEWE, was tested interms of the output voltage and output power density at a varying concentration of HCC solution (0.9-1.5 M NH₄HCO₃). The APEWE unit equipped with novel catalysts based on Reduced Graphene Oxide (RGO) is operated at a varying temperature (50-80 °C). The use of thermally regenerative NH₄HCO₃ solution in the proposed system allows the conversion of low-grade waste heat into electricity in a closed loop with simultaneous production of hydrogen driven by a non-intermittent renewable energy.

2. Materials and methods

2.1 Reverse Electrodialysis

Figure 1a shows the SGP-RED system used in the present study. A RED stack with 20 cell pairs, constructed by modification of commercially available electro dialysis stack (PCCell, Heusweiler Germany), was used for experimental tests. The stack consisted of a total active membrane area of 0.82 m², a projected surface area of 207 cm², and a channel thickness of 0.5 mm. The electrodes used were Titanium mesh coated with Platinum/Iridium (Ti Pt/Ir) with a projected area of 207 cm². PC-SK standard CEMs and PC-SA standard AEMs were used in the stack. Table 1 presents the properties of the membranes used in RED stack.

The HCC solution was composed of NH₄HCO₃ solution with concentrations of 1.5 M, 1.2 M and 0.9 M with Low Concentration Compartment (LCC) solution fixed at 0.1 M (salinity ratio of 6-10). The electrode rinse solution composed of 0.3 M K₄Fe(CN)₆, 0.3 M K₃Fe(CN)₆ and 2.5 M NaCl was recirculated at 30 L/h from one electrode compartment to the other electrode compartment and back to its storage vessel.

Electrochemical measurement on RED was performed by loading the system with a high dissipation five-decade resistance box (CROPICO, Bracken Hill, US): DC voltage drop across the load resistors was measured by a 3½ digital multimeter (Velleman, DVM760), and the current by Agilent 34422A 6½ digit multimeter.

Table 1: Properties of ion exchange membranes for RED.

Membrane	Thickness (µm)	Area resistance Ωcm ²	Permselectivity	Anion exchange capacity (meq./g)
PC-SA AEM	200	1.8	>0.95	~0.4-1.1
PC-SK CEM	180	2.5	>0.95	~1.2

The overall performance of RED stack is evaluated in terms of voltage (*V*), current (*I*) and gross power density (*P_d*). According to Ohm's law, the voltage drop is linearly related to the current and the total internal resistance of the stack (*R_i*) as:

$$V = OCV - R_i \cdot I \quad (1)$$

where OCV is Open Circuit Voltage. The power density *P_d* (W/m²MP) and the current density *i* (A/m²) are related as:

$$P_d = \frac{1}{NA} \frac{V^2}{R_u} = \frac{1}{NA} \left(\frac{OCV}{R_i + R_l} \right)^2 R_l = -a \cdot i^2 + b \cdot i \quad (2)$$

where A is the active area of a single membrane, N is the number of cell pairs, R_l is the load resistance, ' a ' and ' b ' are two fitting parameters. According to Eq. 2, P_d reaches its maximum value when $P_{d,max} = b^2/4a$ for a maximum current density $i_{max} = b/2$.

2.2 Alkaline Polymer Electrolyte Water Electrolysis

Figure 1b shows the lab-scale APEWE unit. A single cell APEWE unit operating in a medium of 10 wt% KOH used in the present study is described elsewhere (Tufa et al., 2016). The cell was equipped with a heterogeneous anion-selective membrane composed of inert low-density polyethylene, finely milled anion selective particles and water-soluble poly (ethylene glycol-ran-propylene glycol) (Hnát et al., 2011). The properties of the AEM employed for the APEWE are described elsewhere (Tufa et al., 2016). The cathode was made of Ni foam modified with RGO (Chanda et al., 2015). The anode consisted of bare Ni foam loaded with catalytic film (10 mg/cm²) composed of 85 wt% NiCo₂O₄ catalysts and 15 wt% PTFE binder. The cathode has a very open porous structure and possesses suitable properties for electrolyzers applications. The performance of the prepared catalysts was evaluated by determining the load curves for a cell voltage in the range of 1.5-2.0 V.

The power consumed by the electrolyser (P_e) is given by:

$$HPR = \frac{3600 \cdot I_e \cdot \eta}{zF} \quad (4)$$

$$P_e = \Delta E_{cell} I_e \quad (3)$$

where I_e is the current flowing through the system and ΔE_{cell} is the cell voltage which is set in the range of 1.8-2.0 V at the current density of 1 - 3 kA m⁻² in industrial practice.

The hydrogen production rate (HPR) (mol/h) of the electrolyzers can be calculated using the Faraday's law:

where F is the Faraday's constant (96485 C/mol), z represents the equivalent electrons per mole of hydrogen, η is conversion efficiency factor (Hatzell et al., 2014) and 3600 is a conversion constant (s/h).

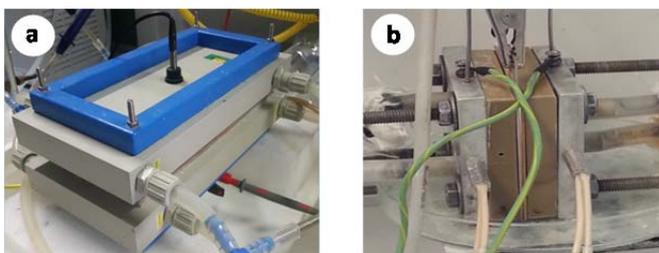


Figure 1: Lab-scale experimental set-up: a) RED and b) APEWE unit.

3. Results and discussion

3.1 Performance of Reverse Electrodialysis

Table 2 summarizes the results for key performance parameters of the RED system operated with NH₄HCO₃ solution. An open circuit voltage (OCV) of 1.24 V was obtained when feeding the RED stack with 0.15 M//0.9 M NH₄HCO₃ solution (salinity ratio of 6). The OCV increased by about 21% (from 1.24 V to 1.50 V) when increasing the HCC concentration from 0.9 M to 1.5 M at LCC concentration of 0.15 M (salinity ratio 10). On the other hand, an OCV of 1.78 V was recorded when using NaCl solution at similar salinity ratio of 10 (0.5 M//5 M). This is mainly due to the lower permselectivity of the membranes in NH₄HCO₃ solution compared to NaCl solutions. For PC-SK CEMs, Geise *et al.* reported a permselectivity of 94.9 % and 75.6 % for NaCl and NH₄HCO₃ solutions (0.1-0.5 M), respectively (Geise et al., 2014). Bicarbonate is more energetically stable in the polymer matrix than chloride due to its greater polarizability compared to chloride. This leads to greater sorption of bicarbonate in the membrane compared to chloride which reduces the membrane permselectivity.

Besides, chloride exhibits greater exclusion compared to bicarbonate due to electrostatic interactions of the densely charged chloride with the membrane matrix (Geise et al., 2014).

Table 2: RED system performance parameters.

RED parameters	NH ₄ HCO ₃ feed solutions		
	0.15 M//0.9 M	0.15 M//1.2 M	0.15 M//1.5 M
OCV	1.24	1.36	1.50
$R_i(\Omega)$	5.6	5.7	5.2
i_{\max} (A/m ²)	5.0	5.4	6.4
$P_{d,\max}$ (W/m ² MP)	0.15	0.17	0.23

Figure 2b presents the power curves for the RED tested with a varying concentration of NH₄HCO₃ solution. A maximum gross power density ($P_{d,\max}$) of 0.15 W/m²MP (MP: Membrane Pair) was measured when feeding the lab-scale RED stack with 0.15 M//0.9 M NH₄HCO₃ solution. The $P_{d,\max}$ increased by 53% (from 0.15 to 0.23 W/m²MP) when increasing the HCC concentration from 0.9 M to 1.5 M (salinity ratio of 10). These variations were accompanied by an increase of i_{\max} from 5.0 to 6.4 A/m². Under similar conditions i.e. salinity ratio of 10, a $P_{d,\max}$ of 0.85 W/m²MP was obtained for RED tested with NaCl solutions (0.5//5 M). This difference in performance between the NaCl-based RED and AmB-based RED operations is mainly attributed to the difference in electrochemical properties of membranes in NaCl and AmB solutions. The area resistances of the AEMs in AmB are greater than those in NaCl. This contributes to the overall internal stack resistance which leads to a reduction in the performance of AmB-based RED. In fact, the low area resistance of AEMs in AmB can be overcome using optimally designed membranes, for example, by tuning membrane swelling properties using a reinforcing material.

With the aim to demonstrate the concept of a novel, thermally driven electrochemical generator combining a RED stack and a distillation column, Luo *et al.* (Luo et al., 2012) investigated the potential of NH₄HCO₃ for electricity generation using RED. A $P_{d,\max}$ of 0.66 W/m²MP was recorded for a test employing NH₄HCO₃ solution of 0.02 M//1.5 M at a flow rate of 800 mL/min.

The concept proposed in the present study using thermally regenerative NH₄HCO₃ for SGP generation presents a profound basis not only for conversion of low-grade heat into electrical power in a closed loop, but also renewable hydrogen production using non-intermittent power source.

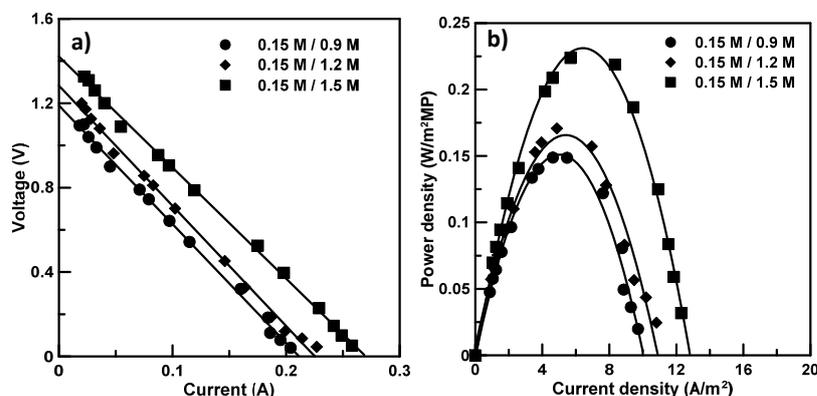


Figure 2. a) Voltage vs current curves for the SGP-RED stack tested at a varying concentration of NH₄HCO₃ HCC solution (0.9-1.2 M); b) Power density vs current density curves for the SGP-RED stack tested at a varying concentration of NH₄HCO₃ HCC solution (0.9-1.2 M); HCC solution of 0.15 M, 20 cell pairs, flow velocity of 0.7 cm/s, 25 °C.

3.2 Alkaline polymer electrolyte water electrolysis

Figure 3a presents the load curves of the alkaline water electrolyzer at a varying temperature. At a 15% w/w binder loading, the current density increased by 20% (from 150 to 182 mA/cm²) when increasing the temperature from 50 °C to 80 °C. On average, the increase of current density was 1.1 mA/cm² per °C. Temperature increases the cell performance through the enhancement of the electrochemical reaction rate and the reduction of the electrode over potential. Investigation of the influence of temperature on polymer

electrolyte membrane (PEM) water electrolysis resulted in about 20% increase of current density when increasing the temperature from 42 to 58 °C at cell voltage greater than 1.8 V and pressure of 7 bar (Santarelli et al., 2009).

Thus current density for the water electrolysis reported in the present study is generally higher than our previous study, which reached a maximum of about 120 mA/cm² at 65 °C, however, with the use of catalysts based on spinel oxides. The use of RGO-modified nickel foam electrode here allows an excellent hydrogen evolution reaction (HER) catalyst in alkaline medium, even surpassing the Pt-C catalyst in terms of HER activity. At a cell voltage of 1.85 V, experimental tests on APEWE system resulted in a current density of 54 mA/cm² when using a Ni foam cathode and 210 mA/cm² when using a Pt-C-modified Ni foam, whereas a current density of 223 mA/cm² was recorded when using RGO-modified Ni foam as a cathode under identical conditions (Chanda et al., 2015).

3.3 Hydrogen production rate

Figure 3b shows the hydrogen production rate of the APEWE unit at a varying temperature and electrolyzer efficiency. The hydrogen production rate varies directly with the temperature at a rate of 54.7 cm³/cm².h per °C. A value of 60 cm³/cm².h, corresponding to 2.2x10⁻³ mol H₂/cm².h, was recorded at 50 °C and an electrolyzer efficiency of 80%, which increased to a maximum of 66.4 cm³/cm².h, corresponding to 2.7x10⁻³ mol H₂/cm².h, at 80 °C and an electrolyzer efficiency of 80%. A maximum value of 74.7 cm³/cm².h, corresponding to 3.07x10⁻³ mol H₂/cm².h, is reached at 80 °C and an electrolyzer efficiency of 90%. Reduction of electrode overpotential and an increase of solution conductivity account for the improved performance of the electrolyzer with rising temperature.

The hydrogen production rate reported here is very high, even superior to the case of using noble electrocatalysts. As mentioned earlier, this is mainly attributed to the excellent electrocatalytic activity of the employed RGO implying a viable strategic approach for commercial feasibility of the proposed system.

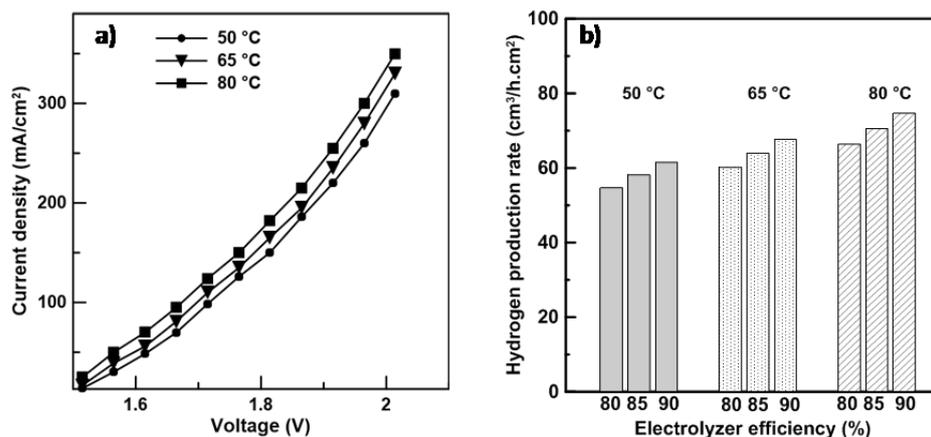


Figure 3: a) Load curves of the alkaline water electrolysis; b) Hydrogen production rate (HPR) of the electrolyzer at different temperature (50, 65 and 80 °C); Separator: heterogeneous anion selective polymer electrolyte membrane; Anode: Ni foam modified with platinum group metal (PGM)-free electrocatalysts; Cathode: Ni foam modified with an electrochemically RGO; Polytetrafluoroethylene (PTFE) binder (85% w/w catalyst and 15%w/w PTFE); geometric electrode area: 4 cm²; Electrolyte flow rate 5 mL/min.

4 Conclusions

An APEWE driven by a SGP-RED operating with a thermolytic solution (NH₄HCO₃) can be a viable strategy for utilization of low-grade waste heat for hydrogen production. Although the SGP-RED system presented in this study reached a maximum power density of only 0.23 W/m²MP when using 0.15 M//1.5 M NH₄HCO₃ feed solutions, there is huge potential to improve this power density through further optimization of the materials and the processes. For instance, the use of well-designed membranes with low resistance and improved permselectivity when contacted with NH₄HCO₃ feed solutions can alleviate this challenge.

On the other hand, a promising result in terms of hydrogen production rate was recorded from APEWE unit mainly attributed to the use of RGO modified Ni cathode which facilitates the formation of free active sites on the Ni phase, thereby enhancing the HER. However, the performance of APEWE can be further improved by using highly conductive and durable membranes as well as polymer binders.

Further development of new materials and optimization of processes for high efficiency in both RED and APEWE is currently ongoing under an EU-funded MARVEL (Novel Material and Process Design for Reverse Electrodialysis-Water Electrolysis Energy System) project. Such energy system driven by the SGP either from NaCl-based salts or AmB-based salts is highly beneficial from the point of view of inexhaustive power generation and hydrogen production, allowing the conversion of low-grade waste heat into electricity as well as hydrogen in a closed loop.

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