Comparison of hydrogen production and electrical power generation for energy capture in closed-loop ammonium bicarbonate reverse electrodialysis systems†

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Currently, there is an enormous amount of energy available from salinity gradients, which could be used for clean hydrogen production. Through the use of a favorable oxygen reduction reaction (ORR) cathode, the projected electrical energy generated by a single pass ammonium bicarbonate reverse electrodialysis (RED) system approached 78 W h m⁻³. However, if RED is operated with the less favorable (higher overpotential) hydrogen evolution electrode and hydrogen gas is harvested, the energy recovered increases by as much 1.5 x 118 W h m⁻³. Indirect hydrogen production through coupling an RED stack with an external electrolysis system was only projected to achieve 35 W h m⁻³ or 1/3 of that produced through direct hydrogen generation.

Introduction

The development of novel decarbonized methods of renewable energy generation has become increasingly important as atmospheric CO₂ concentrations approach 400 ppm.1–3 Estuarial salinity gradient energy, released when river and seawater mix, represents nearly 1.9 TW of unexploited clean energy.4–13 The primary technologies capable of capturing this energy are pressure retarded osmosis (PRO), reverse electrodialysis (RED) and capacitive mixing (CapMix).14–16 Each technology has a unique approach for energy conversion, but the usable energy produced has been limited to electrical energy. The use of RED uniquely enables continuous and direct electrical current generation that could be used to produce a variety of products such as hydrogen gas.

Within a RED stack, series of ion exchange (anion and cation selective) membranes separate solutions with different chemical potentials (e.g. river water and seawater). This concentration gradient allows a Donnan or membrane potential to form at each membrane interface. By increasing the number of membranes, the overall potential rises, driving electrochemical reactions and current generation at the surrounding electrodes. In most RED studies, reversible redox couples (e.g. Fe²⁺/Fe³⁺ or [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻) are used to reduce the number of membranes needed to overcome the electrode reaction overpotentials.6,17 Alternatives are precipitating/dissolving electrodes,16,18,19 gas (H₂/O₂/Cl₂) generating electrodes8,18–23 and capacitive electrodes.24 Many of these reactions are either unfavorable and consume energy, or are impractical for large scale systems.

Two electrodes which may present unique opportunities for energy production using RED are oxygen reduction, and hydrogen evolution. The oxygen reduction reaction (ORR) could enable current production without consumption of significant amounts of energy (low overpotential). The use of a passive air breathing cathode system would avoid energy needed for solution aeration using dissolved oxygen or catholyte regeneration. Only one RED system has been operated with an ORR cathode, but a thorough evaluation of the electrode overpotentials was not conducted.19 Cathodes based on the hydrogen evolution reaction (HER) have been considered to be disadvantageous for RED systems due to high overpotentials. However, if the hydrogen gas generated is harvested, there is a possibility for energy production that has not been previously recognized. Hydrogen gas has primarily been viewed as a waste gas produced during electricity generation in RED systems, but RED has never been intentionally used or optimized as a method for renewable hydrogen gas production.

The potential for energy capture using either oxygen reduction or hydrogen evolution was investigated here using ammonium bicarbonate (AmB) solutions. Thermolytic solutions such as AmB have recently been examined as a method to enable energy production from salinity gradients in closed-loop systems.9,25–28
AmB is an excellent chemical for creating salinity gradients from waste heat because it has a low temperature decomposition point, which allows it to be distilled to CO₂ and NH₄ to form high and low concentration solutions that can be used for salinity gradient energy production. AmB has an additional advantage compared to NaCl solutions because its use reduces electrode overpotentials for both HER and ORR.²⁶,²⁷ Thus, AmB may make these reactions more favorable for energy production than previously achieved using river water and seawater in RED systems. Energy production using an AmB solution was examined under five general scenarios: (1) simultaneous electrical and hydrogen generation with an HER cathode operated at the limiting current; (2) electricity generation with an ORR cathode operated at the limiting current; (3) simultaneous electrical and hydrogen generation at an HER cathode operated at the peak power; (4) electricity generation with an ORR cathode operated at peak power; and (5) indirect hydrogen generation using an ORR based RED to power a separate water electrolysis cell. For direct hydrogen gas production, the use of a non-precious metal catalyst (MoB) and a bifunctional electrocatalyst (Pt/Ir) was also examined.

Materials and methods
Reverse electrodialysis stack
A 20 cell pair RED stack was constructed by modifying a commercially available electrodialysis stack (PCCell, Heusweiler Germany). This unit has a total active membrane area of 0.87 m², a projected surface area of 207 cm², and each cell pair was 0.5 mm thick. The anolyte volume was 80 mL, and the anode was titanium mesh coated with platinum/iridium (Ti Pt/Ir) with a projected area of 207 cm². The system was modified to use two different cathode endplates. One was completely sealed and used for the HER reaction for hydrogen gas production, while the other one contained an open area to enable passive oxygen diffusion to an ORR cathode (Fig. 1A and B). The exposed area with the open endplate was ~ 175 cm². Anolyte and catholyte solutions (1 M AmB) were each recycled separately at 100 mL min⁻¹. The 10 L high concentration solution (1.5 M AmB) was continuously recycled through the stack, while the 20 L of low concentrate solution (distilled water) was used in a single pass mode (400 mL min⁻¹).

Cathodes
Three different cathodes were used: platinum and carbon (Pt/C) on carbon cloth for both ORR and HER; and Pt/Ir on titanium or molybdenum boride and carbon (MoB/C) on carbon cloth for only HER. The Pt/C cathode was wet proofed carbon cloth (type B, E-TeK) coated with carbon black, Pt (0.5 mg-Pt cm⁻²), and a Nafion binder on the water side, and 4 layers of polytetrafluoroethylene (PTFE) on the air side to prevent water leakage out and to allow passive oxygen delivery for ORR tests.²⁹ During HER tests the PTFE layer was placed against the solid endplate. The two other cathode catalysts, MoB and Pt/Ir were examined as alternatives to Pt for HER. Mo-based catalysts such as MoSₓ, Mo₂C and MoB have shown activity for HER, but MoSₓ is not stable at higher pH. Preliminary electrochemical tests in our lab with AmB have revealed a higher activity with MoB than Mo₂C (data not shown), which might be due to the lack of electrochemical activation for MoB at higher pH.³⁰,³₁ Thus, MoB was tested here as a possible alternative to Pt, with performance compared to the commercially available electrode provided with the test cell (mixed catalyst Pt/Ir on titanium).³² The molybdenum-based MoB cathode was prepared in a similar manner to the Pt cathode, but with a higher catalyst loading (5 mg-MoB cm⁻²), and no PTFE layers. Currently the commercial cost of MoB is 5 $ g⁻¹, whereas for Pt it is 45 $ g⁻¹. Therefore, the higher loading of MoB did make the final cost similar to Pt, but no precious metals were used. In addition, the loading and application of the MoB cathode were not optimized here.

Performance data
Galvanostatic polarization was performed with a multi-channel potentiostat (model 1470E, Solatron Analytical, Hampshire, England), and current was scanned from 0 to 300 mA at 1 mA s⁻¹. Ag/AgCl reference electrodes (BASI, West Lafayette, IN) were placed on either side of the stack in the anolyte and catholyte. Anode, cathode, stack and whole cell potentials were recorded during each sweep. Five to ten polarization curves were recorded to ensure reproducible results. The whole cell power density was calculated as

\[
P_{\text{cell}} = \frac{U_{\text{cell}} \cdot I_{\text{cell}}}{A_{\text{mem}}} \quad (1)
\]
where \( P_{\text{cell}} \) is the electrodes power density (W m\(^{-2}\)), \( U_{\text{cell}} \) is whole cell voltage (V), \( I_{\text{cell}} \) is the whole cell current (A), and \( A_{\text{mem}} \) is the cross sectional area of all the membranes (m\(^2\)). The stack power density, \( P_{\text{stack}} \) which excluded electrode overpotentials, was calculated using eqn (1), but the stack voltage (\( U_{\text{stack}} \)) was used instead of the whole cell. The stack voltage was recorded using reference electrodes located on either side of the stack. The difference (\( P_{\text{stack}} - P_{\text{cell}} \)) was calculated in order to calculate the power consumed at the electrodes.

**Determination of the potential for electrical power generation or hydrogen generation**

Energy production from electrical power generation or hydrogen gas production was evaluated under five cases (Table 1). For cases 1–4, (Fig. 2) the electrical energy generated with various cathodes (ORR and HER) was determined through dividing the electrode peak power density by the volume flow rate, as

\[
E_{\text{e}} = \frac{P_{\text{cell}}}{Q}
\]

(2)

where \( E_{\text{e}} \) is the electrical energy harvested (W h m\(^{-3}\)), and \( Q \) the volume flow rate (m\(^3\) h\(^{-1}\)).

For case 1 & 3 the theoretical moles of hydrogen generated was calculated using

\[
n_{\text{H}_2} = \frac{I \cdot 3600}{zF} \eta
\]

(3)

where \( n_{\text{H}_2} \) is the (moles \( \text{H}_2 \) h\(^{-1}\)), \( I \) the current (A), 3600 a conversion factor (seconds per hour), \( z \) the equivalent electrons per mole of hydrogen, \( F \) is Faradays constant (96 485 C mol e\(^{-1}\)), and \( \eta \) is a conversion efficiency factor (to account for hydrogen gas losses relative to current generation) which was set at 80%.\(^{33}\)

The moles of hydrogen gas were converted to hydrogen energy based on the heating value of hydrogen gas, as

\[
E_{\text{H}_2} = n_{\text{H}_2} \cdot \Delta H_{\text{H}_2} (0.277)
\]

(4)

where \( E_{\text{H}_2} \) is the energy (W h m\(^{-3}\)), \( \Delta H_{\text{H}_2} \) is the high heating value of hydrogen (286 kJ mol \(^{-1}\)), and 0.277 is a conversion factor from kJ to W h.

To calculate the indirect (ex situ) hydrogen generation by a coupled RED–water electrolysis system (case 5), the current corresponding to the RED voltage necessary to drive water electrolysis at 2 V was chosen (Fig. 2, point 4). This current at 2 V corresponds to the maximum electrical current which would be supplied to the electrolysis system from the RED system.

Current was converted to the theoretical moles of hydrogen gas that could be produced using eqn (3), and to energy using eqn (4). The electrolysis efficiency was assumed to be 80%.\(^{33}\)

As RED systems are scaled up in size, and the number of membranes is increased, the fraction of energy consumed at the electrodes is expected to decrease. To capture this scenario, the electrode overpotentials were neglected and the stack performance data (power and current) were used to estimate possible electrical power and hydrogen energy production.

**Energy extracted through batch testing**

To verify that energy predictions based on the smaller number of cells were reasonable, additional batch tests with a 20 cell pair RED with either an ORR or HER cathode were conducted. During these tests, 10 L of high and low concentration solutions were constantly recycled through the stack, and the electrodes were maintained near the limiting current operating using a 2 \( \Omega \) resistor, or the peak power operating point with a 10 \( \Omega \) resistor. The resulting current through the external circuit was used to calculate the total electrical energy generated during the hour-long test as

\[
E_{\text{e}} = \int_{0}^{\infty} \frac{P_{\text{cell}}}{v} \cdot dt
\]

(5)

where \( P_{\text{cell}} \) is the power of the cell, and \( v \) is the volume of solution mixed. The potential hydrogen energy was estimated.

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**Table 1** Different cathode reaction (and catalysts) for energy production from AmB RED. The operating point with which the energy (hydrogen or electricity) was estimated from is also listed

<table>
<thead>
<tr>
<th>Cathode reaction</th>
<th>Cathode catalyst</th>
<th>Operating point from Fig. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1: direct hydrogen and electricity generation</td>
<td>HER</td>
<td>Pt, MoB, Pt/Ir</td>
</tr>
<tr>
<td>Case 2: electricity generation</td>
<td>ORR</td>
<td>Pt, MoB, Pt/Ir</td>
</tr>
<tr>
<td>Case 3: direct hydrogen and electricity generation</td>
<td>HER</td>
<td>Pt</td>
</tr>
<tr>
<td>Case 4: electrical energy generation</td>
<td>ORR</td>
<td>Pt</td>
</tr>
<tr>
<td>Case 5: indirect hydrogen generation</td>
<td>ORR, coupled with electrolysis</td>
<td>Pt</td>
</tr>
</tbody>
</table>
using eqn (3) and (4), assuming cathodic recoveries of 70% or 90%.

Results and discussion

Electrical power generation with oxygen reduction

The maximum power density produced with an ORR cathode was greater than that obtained with the HER cathode (Fig. 3). With 20 cell pairs, the peak power density with ORR reached 0.18 W m\(^{-2}\), whereas with the HER the peak power density was 0.13 W m\(^{-2}\) (\(\approx 33\%\) difference). These values are significantly lower than those typically reported in the literature for RED stacks (\(\approx 0.6 \text{ W m}^{-2}/50 \text{ cell pair}\)) because both the electrode overpotentials were included here in the total power. The stack power density (calculated using reference electrodes) approached 0.45 W m\(^{-2}\), which is similar to other RED stack power densities (Fig. S1, ESI\(^\dagger\)). With 20 cell pairs, the reduction in power due to the electrodes was 61% with the ORR cathode, and 70% with the HER electrode. This difference was further increased to 70% (ORR) and 75% (HER) with 15 cell pairs, and to 89% (ORR) and 93% with 10 cell pairs (HER). There was a linear relationship observed between the difference in power measured between the stack and electrodes, and the cell pair number. As the number of cell pairs increases, this difference is essentially eliminated. It is estimated based on a linear regression of the data here that the difference between the stack and electrodes would be removed with \(~ 40\) cell pairs (80 membranes) with the ORR electrode. With an HER electrode, this difference is not eliminated until \(~ 52\) cell pairs (104 membranes).

The anode potentials were the same in all tests, ranging from 0.9–1.0 V versus NHE, and therefore differences between the power densities were due to cathode performance (Fig. 3B). At low current densities (\(~ 1\) A m\(^{-2}\)) the cathode potentials differed by \(~ 200\) mV. However, at higher current densities (\(~ 10\) A m\(^{-2}\)) this difference increased to nearly 700 mV. This reduction in cathode overpotential by 700 mV accounts for the extra \(~ 10\) cell pairs, or 20 membranes needed for the RED with a HER cathode. With the price of ion exchange membranes limiting practical implementation of large scale RED systems, reducing the number of membranes needed through reducing electrode overpotentials will likely improve the economic and technical feasibility of RED systems.

Evaluating energy generation through H\(_2\) production versus O\(_2\) reduction

The energy extracted per m\(^3\) of low concentrate solution was extrapolated from peak power and the limiting current operating points (Fig. 3). The greatest energy extraction was attained with the highest number of cell pairs (20), and through hydrogen gas generation (Fig. 4). With 20 cell pairs the expected maximum energy extracted through hydrogen gas and electricity production at the systems limiting current was \(~ 10.6\) W h m\(^{-3}\) (with 95% of that energy coming through hydrogen). If a HER based RED was operated at the peak power position, \(~ 9.39\) W h m\(^{-3}\) would be generated, with 4.63 W h m\(^{-3}\) obtained through
electricity and 4.75 W h m$^{-3}$ from hydrogen. With the RED operated with the low overpotential cathode (ORR RED), only 2.8 (limiting current) to ~6.5 W h m$^{-3}$ (peak power) of electrical energy was generated (Fig. 3). This was 28% more electrical energy than produced with the HER RED, but overall 36% less energy than produced through hydrogen. However, the total energy extracted through each system would remain similar, as the H$_2$ would eventually need to be converted to electricity through a fuel cell which typically operates with 50–80% energy efficiency.

In order to estimate the energy that could be extracted using a stack with a larger number of cell pairs which incorporated either the ORR or HER cathode, a linear regression was applied to the plots in Fig. 4. For a 100 cell pair stack, 53 W h m$^{-3}$ ($R^2 = 0.97$) was projected to be attainable through direct hydrogen generation, with only 17 W h m$^{-3}$ ($R^2 = 0.99$) through indirect hydrogen generation (electricity generation followed by water electrolysis). In terms of electrical energy generation, 44 W h m$^{-3}$ ($R^2 = 0.98$) was obtained through the use of an ORR cathode and 33 W h m$^{-3}$ ($R^2 = 0.99$) from an HER cathode.

The stack performance data (peak power and limiting current values), which eliminates the impact of electrode over-potentials, were also used to estimate the maximum electrical and hydrogen energy attainable from RED systems (Fig. 5). This was evaluated because with larger systems the potential losses at the electrodes become negligible. With 100 cell pairs ~118 W h m$^{-3}$ ($R^2 = 0.96$) may be obtainable through hydrogen generation (approaching PRO) and only ~78 W h m$^{-3}$ ($R^2 = 0.99$) from electricity. Furthermore, the potential for indirect hydrogen generation was ~3 times less than direct hydrogen production, only producing ~35 W h m$^{-3}$ ($R^2 = 0.97$).

Batch recycle tests conducted with 10 L of low concentrate showed that significantly more energy could be generated through hydrogen production with the cathode operated near the limiting current (Fig. 6). In addition, with a low concentration recycle, the potential energy extracted assuming a cathodic recovery of 70% approached 25 W h m$^{-3}$. This was an increase of ~135% when compared to performance predicted with a 20 cell pair HER-RED stack with no recycle. One difference observed between the batch recycle tests and the predictions based on the performance data was a slight decrease in electrical energy extracted at the peak power position, rather than at the limiting current. This was likely due to the fact that a fixed resistance had to be used during the batch recycle tests, and thus as the system resistance changed (was reduced), the cell would approach the peak power position.

**Evaluation of low cost catalyst for hydrogen evolution**

When MoB was used as the cathode catalyst instead of Pt, the limiting current density decreased from 10 A m$^{-2}$ to 8 A m$^{-2}$ (Fig. 7A). When the current collector was changed from a carbon cloth to titanium, and the catalyst was Pt/Ir, current density was further decreased to 7 A m$^{-2}$. This was due to the ~150 mV difference between the MoB cathode and the Pt cathode (Fig. 7B), and the nearly 500 mV difference between the Pt and the Ti (Pt/Ir).

With these alternative catalysts, the energy captured through hydrogen from the various cathodes decreased to 10.2 W h m$^{-3}$ with MoB, and to 8.9 W h m$^{-3}$ with Ti (Pt/Ir), compared to 12.6 W h m$^{-3}$ with Pt. If these results are extrapolated to 100 cell pairs, the projected energy extracted through the MoB and Ti (Pt/Ir) electrodes was ~56 W h m$^{-3}$ and 35 W h m$^{-3}$ (Fig. S2, ESI†). Thus, the MoB electrode only produced 16% less energy than the Pt, making it a potentially viable alternative to hydrogen generation.

The main advantage of using RED for renewable hydrogen gas production, is the higher value product (i.e. self powered H$_2$ gas generation). Today, 10–11 million metric tons of hydrogen
are produced each year in the United States with a majority of this hydrogen used at industrial sites. With the average price of this hydrogen around $10 kg\(^{-1}\) this represents a market value of nearly $150 billion. Last year in the United States, industrial sites used 980 billion kW h of electricity, which on average cost $0.1 kW h\(^{-1}\), accounting for a market value of $98 billion. While both electricity and hydrogen production are large markets, renewable technologies which are capable of directly producing hydrogen are limited. Thus, RED may be able to better compete with other renewables in the energy sector, through direct hydrogen production.

Conclusions

To date, hydrogen generation in RED systems has been avoided due to high overpotentials which cause a reduction in the electrical power generation. However, if hydrogen gas can be recovered, a hydrogen generating RED can produce \(\sim 118\) W h m\(^{-2}\), or 1.5× more energy than that derived solely through electricity. The value of the combined product is also estimated to have an \(\sim 27\%\) greater value than electricity alone. Furthermore, this hydrogen gas production is carbon neutral and can be produced without any electrical grid based energy. For renewable electricity generation, the ORR cathodic reaction was shown to reduce overpotentials by as much as 700 mV, and electrical energy generation was increased by \(\sim 40\%\) compared to a RED stack with HER. The MoB catalyst shows significant promise as a low cost HER catalyst in this RED system, with overpotentials that were only \(\sim 0.1\) V greater than Pt in the AmB electrolyte.

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References