Simultaneous Hydrogen Generation and Waste Acid Neutralization in a Reverse Electrodialysis System

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ABSTRACT: Waste acid streams produced at industrial sites are often co-located with large sources of waste heat (e.g., industrial exhaust gases, cooling water, and heated equipment). Reverse electrodialysis (RED) systems can be used to generate electrical power and hydrogen gas using waste heat-derived solutions, but high electrode overpotentials limit system performance. We show here that an ammonium bicarbonate (AmB) RED system can achieve simultaneous waste acid neutralization and in situ hydrogen production, while capturing energy from excess waste heat. The rate of acid neutralization was dependent on stack flow rate and increased 50X (from 0.06 ± 0.04 to 3.0 ± 0.32 pH units min⁻¹ m⁻² membrane), as the flow rate increased 6X (from 100 to 600 mL min⁻¹). Acid neutralization primarily took place due to ammonium electromigration (37 ± 4%) and proton diffusion (60 ± 5%). The use of a synthetic waste acid stream as a catholyte (pH ≈ 2) also increased hydrogen production rates by 65% (from 5.3 ± 0.5 to 8.7 ± 0.1 m³ H₂ m⁻³ catholyte day⁻¹) compared to an AmB electrolyte (pH ≈ 8.5). These findings highlight the potential use of dissimilar electrolytes (e.g., basic anolyte and acidic catholyte) for enhanced power and hydrogen production in RED stacks.

KEYWORDS: Reverse electrodialysis, Ammonium bicarbonate, Hydrogen evolution reaction, Waste acid neutralization

INTRODUCTION

Energy recovery during waste disposal is growing in importance at industrial sites. Current industrial pollution control practices used to treat waste acids are based on pH neutralization, which requires mixing the acid with a basic or salt solution (carbonate or bicarbonate) and generates heat. Capture of this wasted energy, in a useable form (electricity or electrical power and hydrogen gas using waste heat-derived solutions. A combined RED–distillation system creates a “closed loop” process, limiting the volume of solutions needed and the overall system size. The use of synthetic thermolytic solutions may also avoid some of the disadvantages with natural waters, such as the need for energy intensive pretreatment processes, fixed solution salt concentrations, membrane fouling, and geographic constraints relative to the availability of the source waters. There is also the potential to produce and harvest hydrogen gas, as chlorine evolution is no longer an issue. With the growing need to develop innovative solutions for industrial waste heat and waste acid recovery, an AmB–RED system could be an effective electrochemical method to neutralize acid and recover waste heat as either electricity or hydrogen from excess waste heat. The rate of acid neutralization was dependent on stack flow rate and increased 50X (from 0.06 ± 0.04 to 3.0 ± 0.32 pH units min⁻¹ m⁻² membrane), as the flow rate increased 6X (from 100 to 600 mL min⁻¹). Acid neutralization primarily took place due to ammonium electromigration (37 ± 4%) and proton diffusion (60 ± 5%). The use of a synthetic waste acid stream as a catholyte (pH ≈ 2) also increased hydrogen production rates by 65% (from 5.3 ± 0.5 to 8.7 ± 0.1 m³ H₂ m⁻³ catholyte day⁻¹) compared to an AmB electrolyte (pH ≈ 8.5). These findings highlight the potential use of dissimilar electrolytes (e.g., basic anolyte and acidic catholyte) for enhanced power and hydrogen production in RED stacks.

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hydrogen. This may be most possible at steel, iron, and petroleum industries, as there is typically an excess of both waste heat and waste acid solutions.

The objectives of this study were to develop a new method to treat a low pH waste stream (acid) and to advance the performance of the RED system for capturing waste heat energy. The efficiency and performance of this waste acid disposal process were evaluated by varying stack and catholyte flow rates and using a 2-D transport model to identify the relative contributions of different ion transport mechanisms (electromigration, diffusion, and reaction) to acid neutralization. To study the electrochemical effect of using an acidic catholyte, the RED whole cell and anode and cathode performances were characterized using galvanostatic polarization curves with acidic, basic, and neutral electrolyte solutions (AmB). AmB was used in place of water in the electrolyte rinse solutions. The electrolyte rinse bottle. The composition of gas sample was analyzed for H2, N2, and CO2 using a gas chromatograph (GC, model 310 SRI Instruments argon carrier gas, NV), and the gas volume was calculated using the headspace volume. The hydrogen recovery was with simultaneous hydrogen production and waste acid neutralization.

**Acid Neutralization.** To evaluate the effect the stack flow had on the rate of acid neutralization, the RED stack was operated for 15 min at different stack flow rates of 100, 200, 400, or 600 mL min⁻¹, while the electrolyte rinse chamber flow rates were fixed at 150 mL min⁻¹. During the test, the stack was maintained at a fixed external resistance (10 Ω), and the voltage across the resistors was measured every second. The catholyte solution contained 0.01 M HCl (Sigma-Aldrich, Sigma-Aldrich, St. Louis MO) (pH ~ 2.0), and the anolyte contained 1.4 M AmB. The rate of neutralization was calculated as

\[ r_t = \frac{-\log([H^+_{out}]/[H^+_{in}])}{t} \]  

(1)

where \([H^+_{out}]\) is the concentration of protons in the catholyte at the end of testing, \([H^+_{in}]\) is the initial concentration of protons in the catholyte, and \(t\) is the duration of the experiment. The electrochemical efficiency for acid neutralization, which accounted for the acid neutralization process that occurred through the consumption of protons at the cathode (2H⁺ + 2e⁻ → H₂), was calculated using

\[ \eta_{\text{acid}} = \frac{vF([H^+_{in}] - [H^+_{out}])}{(\int_{t=0}^{\infty} i(dr))} \]  

(2)

where \(v\) is the volume of acid neutralized, \(F\) is Faraday’s constant (96485 C mol⁻¹), and \(i\) is current (A). The effect of the catholyte flow rate was investigated with the stack maintained at 400 mL min⁻¹, and the electrolyte flow rate was set to 10, 50, 100, or 150 mL min⁻¹.

**Hydrogen Production Measurements.** During batch tests, all solutions were recycled in a closed loop. The hydrogen produced over the complete batch cycle was measured by sampling the headspace of the electrolyte rinse bottle. The composition of gas sample was analyzed for H₂, N₂, and CO₂ using a gas chromatograph (GC, model 310 SRI Instruments argon carrier gas, NV), and the gas volume was calculated using the headspace volume. The hydrogen recovery was calculated through comparing the measured hydrogen produced to the theoretically hydrogen produced based on the measured current, as

\[ r_H = \frac{(\eta_F)\eta_{H_2}}{(\int_{t=0}^{\infty} i(dr))} \]  

(3)

where \(\eta_{H_2}\) is the moles of hydrogen recovered in the headspace, and \(\eta_F\) is the moles of charge required per mole of product (H₂) produced.

**Transport Modeling.** The transport of protons from the acidic catholyte to the adjacent HC solutions occurs due to diffusion, electromigration, and convection. In order to distinguish these transport mechanisms, a model of the end membrane, HC chamber, and catholyte was generated based on the Nernst–Planck equation

\[ N_i = -D_i \nabla C_i - z_{i} \mu \nabla \psi + z_{i} \mu \]  

(4)

where \(N_i\) is the total molar flux due to diffusion, migration, and convection. \(D_i\) is the diffusivity of the charge i, \(C_i\) is the concentration, \(z_i\) is the species charge number, \(\mu\) is the species mobility, \(\psi\) the electrolyte potential, and \(\mu\) is the fluid velocity. Fluid velocities were set at the inlets, with values based on those used in the experiments. Constant voltage boundary conditions were set, consistent with the voltage across one membrane, as given by the Nernst equation.
The drop in neutralization indicating other methods of neutralization dominated (Figure 2). Increasing the catholyte flow rate (FR) both in waste acid neutralization performance. Stack and electromigration. Increasing the acid concentration, while influencing the rate of acid neutralization (from 0.06 ± 0.04 to 3.0 ± 0.32 pH units min⁻¹ m⁻²) (Figure 2). Increasing the catholyte flow rates by 1.5x from 10 to 150 mL min⁻¹ resulted in an ∼475% increase in the rate of neutralization (from 0.4 ± 0.09 to 2.3 ± 0.17 pH units min⁻¹ m⁻²).

The increase in the rate of acid neutralization at higher stack flow rates was due to the improved stack performance (power and current) (Figure S1, Supporting Information). An increase in the electrical current enhanced the ionic current, and the rate of ammonium transport into the catholyte. Furthermore, increasing the stack flow rate helped to maintain a high proton gradient across the end membrane, which promoted greater proton diffusion out of the catholyte (Figures S2 and S3, Supporting Information). Higher stack flow rates also increased hydrogen generation rates, which further contributed to acid neutralization (i.e., 2H⁺ + 2e⁻ → H₂). The portion of acid neutralized through the hydrogen evolution reaction was expected to be low, as the neutralization efficiency (a measure of the protons used for hydrogen evolution) after only 15 min was significantly over 100% (e.g., 300% at 150 mL min⁻¹), indicating other methods of neutralization dominated (Figure S4, Supporting Information). The drop in neutralization efficiency during long-term testing (1 h) was observed because all the acid was neutralized early in the batch cycle. A high catholyte flow rate was important for removing the produced H₂ from the cathode surface and into the headspace. By accumulating hydrogen at the cathode, the overall catalyst area decreases, which can reduce the rate of gas evolution.

**Transport Modeling.** Acid neutralization in the RED waste acid disposal system occurred by three different mechanisms: (1) transport of protons from the catholyte into the stack by diffusion, (2) transport of ammonium from the stack into the catholyte to maintain electroneutrality, and (3) proton removal through the production of hydrogen gas. The amount of protons consumed at the cathode and ammonium transported due to electromigration can be estimated using the experimentally obtained current data, using the assumption that for 1 mol e⁻ transported through the circuit, 1 mol of NH₄⁺ will be transported into the catholyte, and 1/2 mol of H₂ is produced. Protons transported across the membrane due to diffusion can be calculated based on a 2-D transport model, where the chemical flux (j = −DdC/dx) is calculated along the length of the catholyte channel (Figure S5, Supporting Information).

Simulations of the ion transport in the RED waste acid disposal system showed that the majority of acid neutralization in the catholyte occurred primarily by diffusion of protons (60 ± 5%) into the stack solution, followed by electromigration of ammonium ions (37 ± 4%). Only a small fraction (≈4%) of the acid neutralization took place through proton consumption at the cathode (Figure 3). This was found in all cases irrespective of the stack and catholyte flow rates (Figure S6, Supporting Information). This result is consistent with the estimate made on the basis of neutralization efficiencies (Figure S4, Supporting Information). The rate of acid neutralization in the RED system was therefore primarily dependent on the existence of a large pH gradient across the end membrane to promote diffusion and electrical current that promoted electromigration. Increasing the acid concentration, while maintaining the membrane surface area and catholyte flow rate, would result in a decrease in the rate of neutralization. Thus, in order to ensure sufficient rates of neutralization, the membrane surface area or catholyte flow rate would need to be increased.

**Reverse Electrodialysis System Performance with Acidic and Basic Catholytes.** Using a basic (NaOH) anolyte
with the AmB catholyte increased the overall power production by 50\% (from 0.06 \pm 0.001 W to 0.09 \pm 0.004 W), compared to tests with AmB as both anolyte and catholyte. Using an acidic (HCl) catholyte with an AmB anolyte increased power by 66\% (0.06 \pm 0.001 W to 0.1 \pm 0.005 W), when compared to a neutral pH AmB electrolyte (anolyte and catholyte) (Figure 4). Using a basic anolyte and an acidic catholyte produced the greatest increase in power of \sim 130\% (0.06 \pm 0.001 to 0.14 \pm 0.004 W), compared with AmB in both electrode chambers. In all tests the stack power density remained constant (0.3 \pm 0.004 W), indicating that the increased performance was due solely to the improved electrode kinetics for hydrogen (cathode) and oxygen (anode) evolution. Reducing the power drop between the stack and whole cell is essential for performance, efficiency, and cost. AmB was used as the neutral pH control because this minimized the crossover of species between the stack and electrolyte solutions.

The improved performance obtained using the acid and base solutions is consistent with improved thermodynamics predicted for the water splitting reaction. On the basis of the Nernst equation, there is an intrinsic relationship between the potential at which hydrogen and oxygen is evolved and the solution pH \( (E_{H^+/H_2} = E^0 - 0.059 \times \text{pH}) \), where \( E^0 \) is the standard potential for hydrogen or oxygen generation. Shifting the pH can aid in reducing the energy consumed to initiate the reaction (hydrogen or oxygen evolution) (Figure S7, Supporting Information). The onset potential for \( O_2 \) evolution decreased by 374 mV with the basic anolyte, when compared to AmB. Likewise, the onset potential for \( H_2 \) evolution increased by 389 mV with an acidic catholyte, when compared to AmB.

These results also highlight the benefits of using dissimilar electrolytes in an electrolysis cell to mitigate electrode overpotential, while avoiding direct crossover of products from the anolyte to catholyte due to the presence of the membrane stack.

**Hydrogen Energy Production.** The hydrogen production rate increased linearly with the stack flow rate \( (R^2 = 98 \pm 1\%; P = 0.01 \pm 0.006) \) (Figure 6). The maximum hydrogen production rate for the synthetic waste acid (WA) catholyte approached 8.7 \pm 0.1 m\(^3\) H\(_2\) m\(^{-3}\) day\(^{-1}\) at 600 mL min\(^{-1}\), which was 65% greater than that produced with AmB (5.3 \pm 0.5 m\(^3\) H\(_2\) m\(^{-3}\) day\(^{-1}\)). With high flow rates the whole cell power and current both increase, which results in elevated hydrogen production rates. The peak power increased by \( >250\% \) (0.016 to 0.061 W m\(^{-2}\)) with an AmB catholyte and by \( >150\% \) (0.033 to 0.083 W m\(^{-2}\)) with an WA catholyte as the stack flow rate was increased from 100 mL min\(^{-1}\) to 600 mL min\(^{-1}\) (Figure S1, Supporting Information). For all flow rates, the WA catholyte produced between 60–90\% more hydrogen than AmB, which was consistent with the increase in whole cell power by 30–90\%.

A reduction in the rate of hydrogen production at the low flow rates was due to a loss of hydrogen gas from the catholyte chamber into the stack. Cathodic recovery of H\(_2\) gas decreased from 70.5 \pm 4\% to 40 \pm 10\% as the flow rate was reduced from

![Figure 4](image1.png)

**Figure 4.** System whole cell (a) polarization curve and (b) power density data with dissimilar electrolytes (AmB, Acid, and base). Stack flow rate was 600 mL min\(^{-1}\) in all tests.

![Figure 5](image2.png)

**Figure 5.** Individual electrode potentials with AmB anolytes, basic anolyte, acidic catholyte, and AmB catholyte with the stack operated at 600 mL min\(^{-1}\).

![Figure 6](image3.png)

**Figure 6.** Measured hydrogen production rate using the waste acid or AmB catholyte.
improve hydrogen gas transfer from the cathode surface. A higher flow rate also improves gas transport from the reactor and into the bottle headspace, which could reduce the loss of hydrogen due to crossover into the membrane stack. High flow rates require more pumping energy, and therefore, developments to mitigate hydrogen losses from the catholyte at low flow rates could improve the overall energy balance.

One major disadvantage to using AmB as a catholyte is the loss of CO₂ from the solution. When an acid solution was used in the catholyte, the product gas was nearly all H₂, but when AmB was used as the catholyte the gas was ~80% CO₂ (Figure S8, Supporting Information). CO₂ if captured can be recycled and used to regenerate stack solutions, but high purity hydrogen is preferable if hydrogen is to be sold or used within fuel cells to generate electricity. It is projected here that the mixed gases could still be valuable, as synthetic gases (syngas) are already used at steel, iron, and petroleum industries for electricity production through combustion or to make valuable products such as synthetic petroleum. Separation of the mixed gases would likely not be a viable method to recovery pure hydrogen as it is too energy intensive.

AmB–RED systems provide opportunities for simultaneous renewable hydrogen production, waste heat conversion, and waste acid neutralization. An AmB–RED system was shown to be effective at neutralizing the waste acid stream, with a rate of neutralization that could be increased nearly 50× by increasing the stack flow rate 6×. Acid neutralization occurred primarily due to diffusion of protons (60 ± 5%) and electromigration of ammonium from the stack into the catholyte (37 ± 4%). Energy recovery through hydrogen increased by as much as 65% by using waste acid as the catholyte, compared to neutral pH AmB solutions.

ASSOCIATED CONTENT
*Supporting Information*
Further electrochemical and modeling analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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