



Junction potentials in thermolytic reverse electro dialysis



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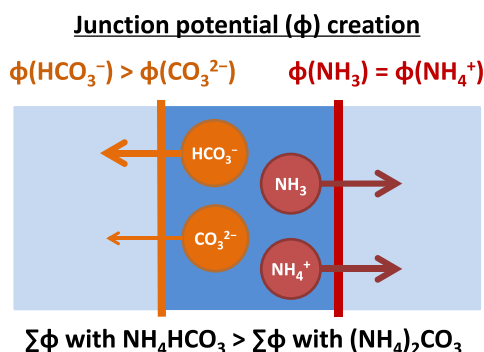
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HIGHLIGHTS

- New method for estimating junction potential of NH_4HCO_3 solution using conductivity
- NH_4HCO_3 solution created greater junction potentials than $(\text{NH}_4)_2\text{CO}_3$ solution.
- Junction potential is not governed by the magnitude of HC but by the ratio of HC/LC.
- Low NH_4^+ by high pH not reducing junction potential across cation exchange membrane
- Instead, total ammonia (both NH_3 and NH_4^+) governs junction potential across CEM.

GRAPHICAL ABSTRACT



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ABSTRACT

Reverse electro dialysis (RED) can produce electric energy from waste heat using thermolytic solutions (e.g., NH_4HCO_3) where waste heat is used to regenerate the high concentration (HC) and low concentration (LC) solutions. The salinity difference between the two solutions in RED is converted into electric potential across an ion exchange membrane (IEM), exploiting the liquid junction potential. Theoretical calculation of the junction potential is cumbersome because the activity coefficients and equilibrium speciation of individual ions are complicated for highly concentrated NH_4HCO_3 solution. We used a simplification of the Planck–Henderson equation to approximate the junction potential in thermolytic RED systems based on conductivity measurements, and this approximation was consistent with experimentally measured junction potentials. The experimental results also found that NH_4HCO_3 created greater junction potentials across anion exchange membranes than $(\text{NH}_4)_2\text{CO}_3$ solution for a given molar concentration ratio. The junction potential was hardly affected by the magnitude of HC as long as the concentration ratio between HC and LC was maintained. Based on the experimental findings, we recommend that thermolytic RED systems be operated under neutral pH and high concentration ratio conditions (above 1:100 ratio). These findings provide information essential for designing and operating thermolytic RED systems for future study and practical application.

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1. Introduction

In reverse electro dialysis (RED), ion exchange membranes (IEMs) are used to create electric power from the salinity difference between two

electrolyte solutions. For instance, the permeation of salt ions in seawater across the IEM into fresh river water generates electric potential energy in an RED stack [1–6]. In addition to seawater and river water, thermolytic solutions (e.g., ammonium bicarbonate solution) can be used in RED for energy recovery from low grade heat sources (often referred to as “waste heat” in various industries) [7,8]. Ammonium bicarbonate vaporizes into gaseous ammonia and carbon dioxide at relatively low

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temperatures (e.g., ~60 °C) [9], allowing easy regeneration of the LC (low concentration) solution by separating ammonia and carbon dioxide using waste heat energy. The separated ammonia and carbon dioxide are used to regenerate the HC (high concentration) solution to maintain sufficiently high concentration of ammonium bicarbonate (e.g., > 1 M) compared to that of the LC solution. The concentration difference between the HC and LC solutions is converted into electric energy in an RED stack of anion exchange membranes (AEMs) and cation exchange membranes (CEMs). This conversion into electric energy is achieved by cations migrating through CEMs and anions through AEMs and eventually by redox reactions at the electrodes. The RED technology coupled with ammonium bicarbonate thermolytic solutions has been recently demonstrated to produce electric energy [7,8,10], H₂ gas [11,12] or CH₄ gas [13] in lab-scale experiments with the aim of eventually recovering energy from low grade waste heat sources in various industries.

The electrical voltage created by the salinity difference across an IEM is a liquid junction potential [15]. Note that although the junction potential across a single IEM is typically small (<0.5 V), the total junction potential is added across an RED stack of hundreds of IEMs, generating a meaningful amount of electric energy. Thus, precise assessment of the junction potential across IEMs is critical for the estimation of electric power generation and energy recovery in RED systems. Theoretical determination of the junction potential requires extensive electrochemical information of individual ionic species. For instance, the equilibrium speciation should be clarified among NH₄⁺, NH₃, H₂CO₃, HCO₃⁻, CO₃²⁻, NH₂COOH (carbamic acid) and NH₂COO⁻ (carbamate) in ammonia- and carbonate-based thermolytic solutions (e.g., ammonium bicarbonate or ammonium carbonate electrolytes). The equilibrium constant is not also clearly defined for carbamate formation (NH₄⁺ + CO₃²⁻ → NH₂COO⁻ + H₂O) and acid dissociation of carbamic acids (NH₂COOH → NH₂COO⁻ + H⁺). In addition, the activity coefficient of these individual ionic species needs to be precisely estimated. To our knowledge, however, many of these electrochemical properties for highly concentrated ammonium bicarbonate electrolytes are unavailable in literature. As a result, accurate theoretical calculation of the junction potential is difficult for RED systems using ammonium bicarbonate solution.

The main objectives of this study are to: (1) leverage an approximation for junction potential which does not require extensive electrochemical information; and (2) verify the equation by comparing it with experimental results. Other important aspects of this study are to: (3) compare two thermolytic solutions (NH₄HCO₃ vs. (NH₄)₂CO₃) for their capacity of creating junction potentials; and (4) investigate the pH and concentration requirements of the HC solution for maximizing energy creation across IEMs. Since thermolytic RED has been recently demonstrated for energy capture with waste heat recovery [8,9,12–14], there is insufficient experimental information to explain the effect of the relative amount of ammonia and carbonate species in thermolytic solutions (e.g., NH₄HCO₃ vs. (NH₄)₂CO₃) on energy recovery. Also, previous studies on thermolytic RED have used relatively high ammonium bicarbonate concentration (0.95–1.7 M) for the preparation of the HC solution [8,9,11,16,17]. In this study, we examined whether such high concentration is necessary for effective energy production in thermolytic RED.

2. Methodology

2.1. Theoretical background: junction potential across an IEM

The electrochemical potential of an ionic species *i* ($\bar{\mu}_i$) is defined as [15]:

$$\bar{\mu}_i = \bar{\mu}_i^0 + RT \ln a_i + z_i F \phi \quad (1)$$

$\bar{\mu}_i^0$ is the standard state electrochemical potential, *R* is the gas constant, *T* is the temperature, *a_i* is the activity of the ionic species, *z_i* is the charge, *F*

is the Faraday constant and ϕ is the electric potential. When two electrolytes of a high concentration (HC) and lower concentration (LC) are located on opposite sides of an IEM, the magnitude of the electric potential difference across the IEM (i.e., the junction potential, ϕ_{jct}) can be found by equating Eq. (2) for all ionic species present in the electrolytes as [15]:

$$|\phi_{jct}| = \frac{RT}{F} \sum_i \frac{t_i}{z_i} \ln \frac{a_i^{HC}}{a_i^{LC}}. \quad (2)$$

The transport number or transference number (*t_i*) is defined as the fractional contribution of an individual ionic flux to the total electric current across the junction (i.e., IEM). Theoretical estimation of the junction potential using this equation needs extensive information of the physical and chemical properties for both the electrolyte and IEM, such as the activity of individual ions and their transport number in the IEM. For highly concentrated ammonium bicarbonate solutions, it is cumbersome to determine the concentration and activity coefficient of individual ion species: NH₄⁺, HCO₃⁻, CO₃²⁻ and NH₂CO₂⁻. In addition, the transport number of these ions in IEMs needs extensive experimental information for membrane permselectivity and competitive partitioning among these ions. As a result, Eq. (2) is not convenient for practical estimation of the junction potential in ammonium bicarbonate-based RED systems. Thus, we propose using the Planck–Henderson equation for junction potentials [15,18–23], which approximates Eq. (2) by assuming that the activity of each species is proportional to the product of molar concentration (*C_i*) and ionic mobility (*u_i*) and that there is a linear transition in concentrations from the HC to the LC:

$$\phi_{jct} \approx \frac{RT}{F} \frac{\sum |z_i| u_i [C_i^{LC} - C_i^{HC}]}{\sum |z_i| u_i [C_i^{LC} - C_i^{HC}]} \ln \frac{\sum |z_i| u_i C_i^{HC}}{\sum |z_i| u_i C_i^{LC}}. \quad (3)$$

Since the transport number of each species is defined by Eq. (4) [15] and the electrical conductivity (κ) of the solution is written as Eq. (5) [15], then Eq. (3) can be further simplified to Eq. (6).

$$t_i = \frac{|z_i| u_i C_i}{\sum |z_j| u_j C_j} \quad (4)$$

$$\kappa = F \sum |z_i| u_i C_i \quad (5)$$

$$|\phi_{jct}| \approx \frac{RT}{F} \left(\frac{t_{counter}}{z_{counter}} + \frac{t_{co}}{z_{co}} \right) \ln \frac{\kappa^{HC}}{\kappa^{LC}} \quad (6)$$

The subscript *counter* denotes the counter-ions that are preferentially transported through an IEM while the subscript *co* is the co-ions that are rejected by the IEM. For instance, for a CEM (cation exchange membrane), NH₄⁺ is the counter-ion and HCO₃⁻, CO₃²⁻ and NH₂CO₂⁻ are the co-ions in ammonium bicarbonate electrolytes, and vice versa for an AEM (anion exchange membrane). For an ammonium bicarbonate concentration between 0.001 and 2 M, measured pH was between 7.9 and 8.1 (Fig. 1), indicating that the fraction of CO₃²⁻ is negligible compared to that of HCO₃⁻ (*pK_a* of HCO₃⁻ is 10.3) [24]. Thus, we approximated all ionic species in the ammonium bicarbonate electrolyte (i.e., NH₄⁺, HCO₃⁻, NH₂CO₂⁻) as monovalent, making *z_{counter}* and *z_{co}* either +1 or -1.

Eq. (6) can be used to estimate the junction potential across a stack of ion exchange membranes in RED for waste heat energy recovery as electricity. By finding the junction potential using Eq. (6), the maximum amount of energy available from two thermolytic solutions can be determined, allowing evaluation of energy recovery in a thermolytic RED system. Eq. (6) can also be used as a tool for modeling energy recovery and conductivity change in a thermolytic RED system.

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