

Supporting Information

Energy Efficient Ammonia Recovery in an Up-scaled Hydrogen gas Recycling Electrochemical System

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Calculations

The cell voltage (E_{Cell} ; V) of the HRES acts as the driving force for the redox reactions (equilibrium voltage) at the electrodes (E_{eq} ; V) and to overcome the internal voltage loss of the system (E_{int} ; V).

$$E_{Cell} = E_{eq} + E_{int} \quad (S1)$$

The internal voltage loss is composed by the anode overpotential (η_{anode} ; V), cathode overpotential ($\eta_{cathode}$; V), ionic losses (E_{ionic} ; V), and the transport losses ($E_{transport}$; V) of ions across the membranes

$$E_{Cell} = E_{eq} + E_{int} = E_{eq} + \eta_{anode} + \eta_{cathode} + E_{ionic} + E_{transport} \quad (S2)$$

The equilibrium voltage is determined by the difference between the anode and cathode potential

$$E_{eq} = E_{cat} - E_{an} \quad (S3)$$

The anode potential (E_{an} ; V) of the hydrogen oxidation reaction (HOR) was determined using:

$$E_{an} = E^0_{an} - \frac{RT}{2F} \ln \left(\frac{pH_2}{[H^+]^2} \right) \quad (S4)$$

Where E^0_{an} is the standard anode potential for hydrogen oxidation (0 V vs NHE), R is the ideal gas constant (8.3144 J/mol/K), T is the absolute temperature (298.15 K), 2 is the amount of electrons transferred, F is the Faraday constant (96,485 C/mol), pH_2 is the calculated hydrogen partial pressure (atm), and $[H^+]$ is the proton concentration at the anode assuming a pH of 0.26, corresponding to a proton concentration of 0.54 M in a fully saturated Nafion membrane ¹

The cathode potential (E_{cat} ; V) of the hydrogen evolution reaction (HER) was determined using:

$$E_{cat} = E^0_{cat} - \frac{RT}{2F} \ln(pH_2[OH^-]^2) \quad (S5)$$

Where E^0_{cat} is the standard cathode potential for water reduction in alkaline conditions (0.828 V vs NHE), and $[OH^-]$ is the hydroxide ion concentration at the cathode (calculated from $pOH = pK_w - pH = 14 - 7 = 7$).

The anode overpotential (η_{anode} ; V) was determined from the measured anode potential and the calculated anode potential based on actual conditions

$$\eta_{anode} = E_{an} - E_{anode,measured} \quad (S6)$$

The cathode overpotential (η_{cathode} ; V) was determined from the measured cathode potential and the calculated cathode potential based on actual conditions

$$\eta_{\text{cathode}} = E_{\text{cathode,measured}} - E_{\text{cathode}} \quad (\text{S7})$$

The ionic potential losses (E_{ionic} ; V) were calculated based on the measured conductivity in feed, concentrate and cathode compartment

$$E_{\text{ionic}} = i \times \left(\frac{d_{\text{feed}}}{\sigma_{\text{feed}}} + \frac{d_{\text{concentrate}}}{\sigma_{\text{concentrate}}} + \frac{d_{\text{cathode}}}{\sigma_{\text{cathode}}} \right) \quad (\text{S8})$$

Where i is the applied current (A/m^2), d_{feed} is the thickness of the feed compartment (5×10^{-4} m), σ_{feed} is the conductivity of feed media (S/m), $d_{\text{concentrate}}$ is the thickness of the concentrate compartment (5×10^{-4} m), $\sigma_{\text{concentrate}}$ is the conductivity of concentrate media (S/m), d_{cathode} is the distance of the cathode to the membrane (5×10^{-4} m), σ_{cathode} is the conductivity of cathode media (S/m).

The combined transport losses across the CEM between feed and concentrate compartment and across the AEM between concentrate and cathode compartment were calculated based on the applied cell voltage (E_{cell} ; V), the measured electrode potentials (i.e. E_{anode} , E_{cathode}), the ionic potential losses (E_{ionic} ; V) and the equilibrium voltage (E_{eq} ; V)

$$E_{\text{transport}} = E_{\text{cell}} + (E_{\text{cathode}} - E_{\text{anode}} - E_{\text{ion}} - E_{\text{eq}}) \quad (\text{S9})$$

The TAN recovery (%) was calculated based on the removed TAN from the feed according to

$$\text{TAN recovery} = \frac{\Delta C_{\text{TAN,feed}}}{C_{\text{TAN,influent}}} \times 100 \quad (\text{S10})$$

Where $\Delta C_{\text{TAN,feed}}$ is the change of TAN concentration of the feed during one HRT (g/L) and $C_{\text{TAN,influent}}$ is the measured TAN concentration in the influent (g/L).

The TAN transport rate ($\text{g}_\text{N}/\text{m}^2/\text{d}$) was determined according to

$$\text{Transport rate}_{\text{TAN}} = \frac{\Delta C_{\text{TAN,feed}} Q_{\text{feed}} t_d}{A_M} \quad (\text{S11})$$

Where $\Delta C_{TAN,feed}$ is the change of TAN concentration of the feed during one HRT (g/L), Q_{feed} is the influent flow speed (L/s), t_d is the amount of seconds per day (86400 s/d), and A_M is the CEM surface area (0.04 m²).

The energy demand for TAN recovery (kJ/g_N) was determined from the TAN transport rate and the electrical energy input of the HRES and electrical energy input of the electrolyser according to

$$\text{Energy demand} = \frac{i E_{Cell} t_d + i_2 E_{Cell2} t_d}{\text{transport rate}_{TAN} 1000} \quad (S12)$$

Where i is the current density (A/m²) of the HRES, E_{Cell} is the average cell voltage (V) of the HRES, t_d is the amount of seconds per day (86,400 s/d), i_2 is the applied current density (A/m²) of the electrolyser, E_{Cell2} is the average cell voltage (V) of the electrolyser, $\text{transport rate}_{TAN}$ is the TAN transport rate (g_N/m²/d), and 1000 is the amount of J per kJ.

The transport number (t_i) for all ions was determined to unravel which the ions were responsible for charge transport over the CEM separating the feed and concentrate compartment. The transport number was calculated based on the difference in ion concentration between influent and effluent in the feed compartment related to the produced current

$$t_i = \frac{\Delta C_i z_i F Q_{feed} HRT}{i HRT A_M} \quad (S13)$$

where ΔC_i is the change in concentration (mol/L) of the specific ion (i.e., Na⁺, K⁺, NH₄⁺) during one HRT, z_i is the charge of the ion (-), F is the Faraday constant (96,485 C/mol), Q_{feed} is the influent flow speed (L/s), HRT is the hydraulic retention time (s), i is the applied current density (A/m²), and A_M is the projected membrane surface area (0.04 m²). The transport number for the combination of hydroxide ions and protons was calculated as the difference between the total charge transport over the membrane and the sum of the transport numbers of the cations

$$t_{H^+/OH^-} = 1 - \sum t_i \quad (S14)$$

Reference

- (1) Herrera, O. E.; Wilkinson, D. P.; Mérida, W. J. *Power Sources* **2012**, *198*, 132–142.