

Article

Electrolytic Regeneration of Spent Caustic Soda from CO₂ Capture Systems

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Abstract: The traditional electrochemical caustic soda recovery system uses the generated pH gradient across the ion exchange membrane for the regeneration of spent alkaline absorbent from CO₂ capture. This electrochemical CO₂ capture system releases the by-products H₂ and O₂ at the cathode and anode, respectively. Although effective for capturing CO₂, the slow kinetics of the oxygen evolution reaction (OER) limit the energy efficiency of this technique. Hence, this study proposed and validated a hybrid electrochemical cell based on the H₂-cycling from the cathode to the anode to eliminate the reliance on anodic oxygen generation. The results show that our lab-scale prototype enabled effective spent caustic soda recovery with an electron utilisation efficiency of 90%, and a relative carbonate/bicarbonate diffusional flux of approximately 40%. The system also enabled the regeneration of spent alkaline absorbent with a minimum electrochemical energy input of 0.19 kWh/kg CO₂ at a CO₂ recovery rate of 0.7 mol/m²/h, accounting for 30% lower energy demand than a control system without H₂-recycling, making this technique a promising alternative to the conventional thermal regeneration technology.

Keywords: CO₂ capture; electrolysis; hydrogen cycling; anion exchange membrane; caustic regeneration



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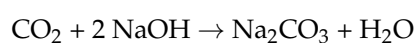


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1. Introduction

Global warming has emerged as one of the major environmental challenges facing the world. Carbon dioxide (CO₂) is the key greenhouse gas that drives global warming and accounts for approximately 55% of observed global warming [1]. The CO₂ concentration in the atmosphere has increased by 3% since 1950 [2]. To combat global warming, deploying carbon capture technologies to reduce the carbon footprint is imperative. Direct air capture (DAC) and point-source capture from existing CO₂ have been extensively reviewed with detailed analysis determining energy efficiency, chemical principle, and commercial viability [3–7].

Several mature carbon capture technologies are commercially available [8–12]. Among these technologies, chemical absorption with alkaline hydroxide solutions (NaOH or KOH) is the most common CO₂ separation method employed by industrial large-scale plants [13,14]. In this process, the CO₂-rich gas stream is pressurised and passed into the absorption tower. The CO₂ dissolves into the liquid phase and chemically reacts with the alkali according to the following reaction:



$$\Delta H^0 = -109.4 \text{ kJ/mol} \quad (1)$$

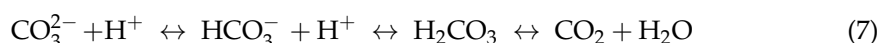
Previous studies showed high capture yields ranging from 90 to 99% [15–17]. After reaching CO₂ saturation capacity, the spent sorbent is regenerated, either by a temperature swing or pressure swing, leading to a high-purity CO₂ gas stream. After CO₂ stripping, the

regenerated CO₂-lean solvent is pumped back into the absorber for another cycle [18,19]. The conventional regeneration of spent sorbent, which implies the conversion of sodium carbonate to sodium hydroxide, requires an energy input of 1.1 kWh/kg CO₂, whereas the thermodynamic minimum energy required is 0.69 kWh/kg CO₂ [20,21]. The comparatively high energy consumption and low regeneration efficiency (<90%) of conventional regeneration technologies [22] necessitate the development of more efficient technologies for CO₂ capture.

Alternative methods have been explored to reduce energy requirements. CO₂ capture and release through an electrochemical process may offer a solution to address these drawbacks. The fundamental of this technology in CO₂ capture relies upon aqueous acid-base neutralisation pathways. An electrochemically generated pH gradient between the cathode and anode chambers is the primary driver for CO₂ capture and recovery. The anode and cathode chambers are typically separated by an Anion Exchange Membrane (AEM) allowing ion migration while providing the individual electrode physical compartments. After CO₂ absorption in an alkaline solution, CO₂ generates carbonate ions. The entire reactions involved in the CO₂ absorption could be written in ionic terms as follows:



The spent sorbent containing HCO₃[−] /CO₃^{2−} is then pumped into the cathode compartment. The (bi)carbonate species migrate through the AEM under an electric field towards the anode compartment. The pH decrease caused by the anodic half-reaction results in the conversion of carbonate to carbonic acid, which then decomposes to form CO₂:



In this context, various cell configurations have been introduced in recent years. An early attempt was made by Walke et al. [23] to separate CO₂ from flue gas using an electrochemical cell to drive CO₂, in the forms of (bi)carbonate species, across an AEM into a CO₂-recovery stream. Another approach used an oxygen cycling electrochemical cell to produce a CO₂-rich effluent from the combustion of fossil fuel [24]. Recently, an alkaline water electrolyser was employed to remove CO₂ from biogas [25]. Mohammadpour et al. [26] developed a three-chamber electrochemical cell that enabled the recovery of CO₂ in an intermediate chamber to prevent CO₂ contamination of the anodic O₂ outlet gas.

Theoretically, the electrolysis of water in standard conditions requires thermodynamic minimum energy of 237 kJ/mol (equivalent to a cell voltage of 1.23 V) [27]. In practice, additional energy is also required to overcome activation overpotential, mainly from intrinsic kinetic barriers associated with half-reactions at each electrode, particularly at the anode [28,29]. Taking all overpotentials into account, the cell voltage of a typical alkaline electrolyser varies between 1.8 V and 2.4 V [30,31]. However, electrolytic H₂ and O₂ formation during pH gradient generation in the electrochemical cell may not be desirable and may present additional obstacles to the CO₂ removal process. For example, co-mixing H₂ and CH₄ when using the alkaline water electrolyser for CO₂ removal from anaerobic digester biogas could present some challenges, including increased probability of ignition, material degradability in contact with H₂, and leakage [32].

Additionally, oxygen formation is a kinetically sluggish reaction that often demands significantly higher voltage compared to the thermodynamic minimum voltage at a given

current density [33]. Therefore, it is necessary to improve the energetic performance of the electrochemical CO₂ capture technique in order to make it competitive and practical. Recently, Muroyama et al. [34] developed an electrochemical hybrid cell powered by H₂ cycling from the cathode to the anode to generate a pH gradient for CO₂ capture from a wide range of gas mixtures. Their approach takes advantage of replacing the oxygen evolution reaction (OER) at the anode with the spontaneous hydrogen oxidation reaction (HOR).

In the hybrid cell, the generated H₂ at the cathode is fed into the anode to substitute the sluggish OER. Each half-cell reaction can be represented as follows:

Cathode:



Anode:



Thermodynamically, this electrochemical cell can be operated at a cell voltage of zero if the hydrogen pressure difference between the cathode and anode side is zero (Nernst equation). However, a wide pH gradient between two compartments required for carbon equilibrium kinetics and overpotentials such as activation and ohmic overpotentials causes an increase in minimum energy requirement.

The previous study demonstrated that CO₂ separation can be achieved using the described electrochemical cycles [34]. However, further research is still required to identify the challenges and explore the potential of this technique for commercial use. Therefore, this study aimed to fill these gaps through a series of experiments to characterise the performance of a lab-scale electrochemical hybrid cell for CO₂ capture. In particular, comparison of the energy demand between the water electrolyser system and the hybrid cell for regeneration of spent alkaline solution for CO₂ capture was conducted. We also identified the effect of key operational parameters, including H₂ loading rate into the anode compartment, back diffusion, and H₂ utilisation rate, on the performance of the electrochemical hybrid cell.

2. Experimental Section

2.1. Materials

All materials were used as delivered without any further treatments (Figure 1). All the chemical reagents used were analytic-grade reagents purchased from Chem-Supply, Australia (Gillman, Australia). A commercial anion exchange membrane (AMI-007, Membranes International Inc., Ringwood, NJ, USA) was used for the experiments carried out in this study. Platinised carbon cloth electrodes with a Pt loading of 0.2 mg/cm² and thickness of 0.365 mm and woven carbon cloth with a microporous layer with a thickness of 0.410 mm were purchased from Fuelcellstore (Bryan, TX, USA). Graphite plates with the serpentine flow field were machined out by Rongxing Group (Zhengzhou, China). Each flow field channel was 50 mm long, 2 mm wide and 3 mm deep. The ribs that formed the channels were 2 mm wide. The Viton[®] fluoroelastomer gasket (Fuel cell store, Bryan, TX, USA) was used in cell fabrication to ensure a good seal.

2.2. Hybrid Cell Fabrication and Testing

The experiments were carried out using a two-compartment apparatus with an active surface area of 25 cm². Two commercial platinised carbon cloth electrodes with a loading of 0.2 mg Pt/cm² (Fuel Cell Store) were employed as the catalytic site of the anode and cathode and were placed against the membrane. A graphite plate with integrated serpentine flow channels (1 mm width and 1 mm depth) was used as the current collector and structural support on the cathode side. Two commercial woven carbon cloths were employed at the anode and cathode as a gas diffusion layer (GDL) to decrease the contact resistance between catalytic sites and the current collector. The whole cell was encased between a graphite plate with flow fields (anode) and a Perspex plate (cathode) using incompressible Polytetrafluoroethylene (PTFE) gaskets. A pocket with a working volume of 50 mL was

manufactured on the cathode Perspex plate to provide a water layer for the H_2 formation reaction. The cell was compressed using 8 bolts and torque value of 5 N.m.

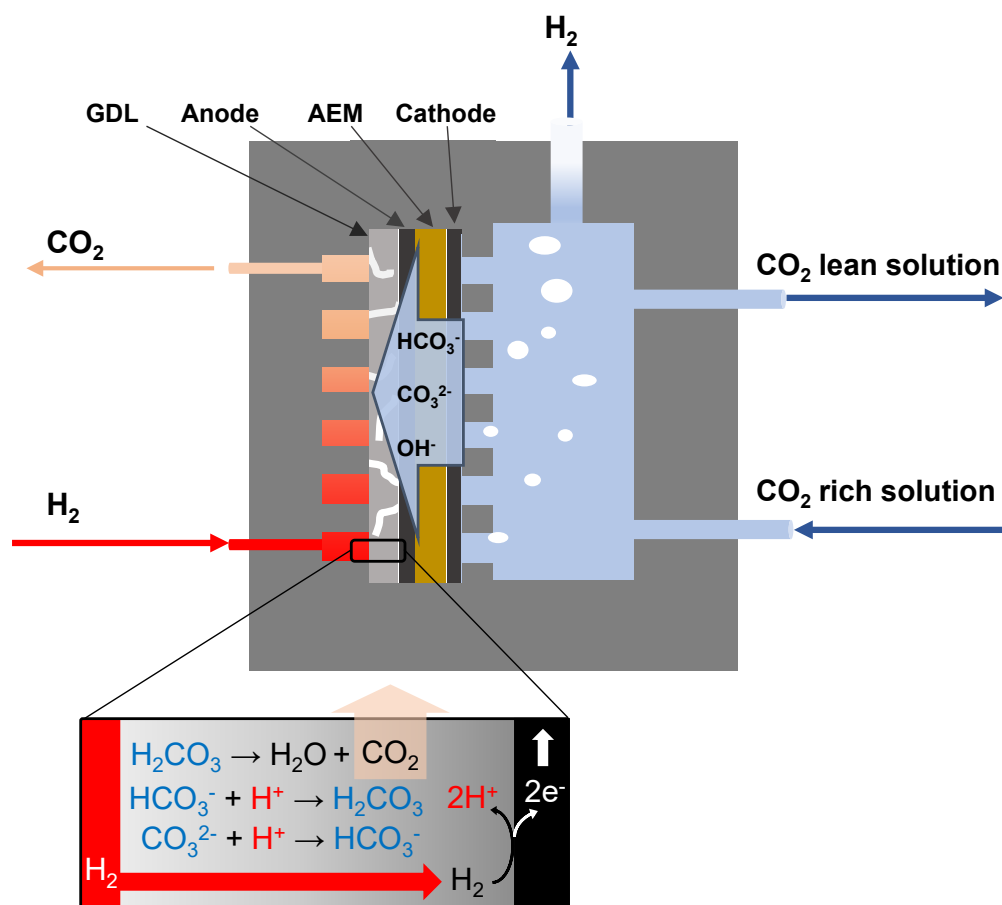


Figure 1. Schematic diagram of the hybrid electrochemical cell for regeneration of spent sorbent used for CO_2 capture.

Tests in this work were conducted with a bicarbonate-rich solution, as each bicarbonate ion molecule carries one CO_2 per one negative charge, thereby it may achieve a high CO_2 diffusional flux to electron ratio for the electrolysis process. The $NaHCO_3$ solution (1 M) was recirculated continuously from a tank to the cathode side by a peristaltic pump to sustain (bi)carbonate concentration.

The membrane was soaked in 0.5 M $NaHCO_3$ solution for 24 h prior to operation. In the hybrid cell mode operation, H_2 gas was fed via a peristaltic pump (7554-95 Masterflex, Vernon Hills, IL, USA) from a non-reactive Tedlar gas sampling bag (CEL Scientific Corp., Santa Fe Springs, CA, USA) into the flow field of the anode side. To avoid dehydration of the membrane, the inlet hydrogen stream to the anode was passed through a humidifier at 50 °C. In the water electrolysis mode, H_2 feed to the anode was replaced by 1 M of $NaHCO_3$ solution. The CO_2 content in the outlet streams was monitored continuously using CO_2 sensors (CO_2 meter GC-0016, Ormond Beach, FL, USA) and accompanying software. A U-tube manometer with oil displacement connected to a Burkert solenoid valve was inserted into the gas outlet line to measure the output gas flow rate to evaluate the Faradaic efficiency and CO_2 relative flux.

The electrochemical cell was coupled with a potentiostat and operated in a three-electrode configuration using a silver–silver chloride ($Ag/AgCl$) reference electrode mounted on the cathode side. A loop control mechanism was developed using LabView™ 2018 version software to control the potentiostat, and pumps and collect the data from the probes and sensors. All experiments were performed at atmospheric pressure and room temperature of

25 ± 1 °C. In accordance with our previous study [35], the integrity of the electrochemical experiments conducted in this work was verified to assure that the data obtained were reproducible with $\leq 10\%$ variation.

2.3. Calculation

To investigate the performance of the experimental setup, some operational parameters such as Faradaic efficiency, relative CO₂ flux and gas permeability of membrane were calculated. Faradaic efficiency was determined based on the H₂ utilisation rate on the anode side as follows (Equation (10)):

$$\text{Faradaic efficiency} = \frac{2 \dot{n}_{\text{H}_2} F}{I} \quad (10)$$

where $\dot{n}_{\text{H}_2}$ is the difference in H₂ molar flow rate (mol/s) between inlet and outlet of the anode. F (96485 A s/mol) is the Faradaic constant and I is the current (A).

The relative CO₂ diffusional flux was defined as (Equation (11)):

$$\text{Relative diffusional flux} = \frac{\dot{n}_{\text{CO}_2} F}{I} \quad (11)$$

where $\dot{n}_{\text{CO}_2}$ is the molar flow rate of CO₂ recovery on the anode side (mol/s).

The H₂ gas permeability of membrane (1 barrer = 10^{-10} cm³ cm cm⁻² s⁻¹ cmHg⁻¹) was defined as:

$$P = \frac{Q_H \times L}{\Delta P_H \times A} \quad (12)$$

where Q_H (cm³/s) is the flow rate of H₂ diffused across the membrane, ΔP_H (cmHg⁻¹) is the partial pressure difference over the length of the membrane, and L (cm) and A (cm²) are the thickness and projected area of the membrane.

The net energy requirement for electrochemical CO₂ separation (kWh/kg CO₂) was calculated using the following equation:

$$E = 0.001 * \frac{IV}{Q_{\text{CO}_2}} \quad (13)$$

where I is the current (A), V is the cell voltage (V), and Q_{CO_2} is the rate of CO₂ regeneration (kg/h).

3. Results and Discussion

3.1. Polarisation Performance

The use of cathodic H₂ as an anodic electron donor is thermodynamically more favourable than the use of water leading to oxygen production. At the same time, cathodic H₂ represents a practical energy source (e.g., in fuel cells). To investigate the practical benefits of sacrificing cathodic H₂ and reusing it as an anodic electron donor, the current–voltage polarisation curves of the described hybrid electrochemical cell were compared with that of an alkaline water electrolyser.

The hydrogen oxidation reaction (HOR) was initiated at about -500 mV for the Pt-loaded electrode, which is close to the equilibrium potential for HOR at pH = 7 (assuming no pH gradient in the vicinity of the anode at which the equilibrium potential of HOR is -414 mV). This means that, in contrast to anodic oxygen production from water splitting, there was no substantial overpotential. The hydrogen oxidation reaction was recognised as a fast electrochemical reaction [36,37], and thus the activation polarisation loss owing to the charge transfer was close to zero. The anodic polarisation curve of the hybrid cell showed a linear behaviour (Figure 2a), indicating that the total overpotential was dominated by ohmic resistance due to ion transport, and the activation overpotential was negligible.

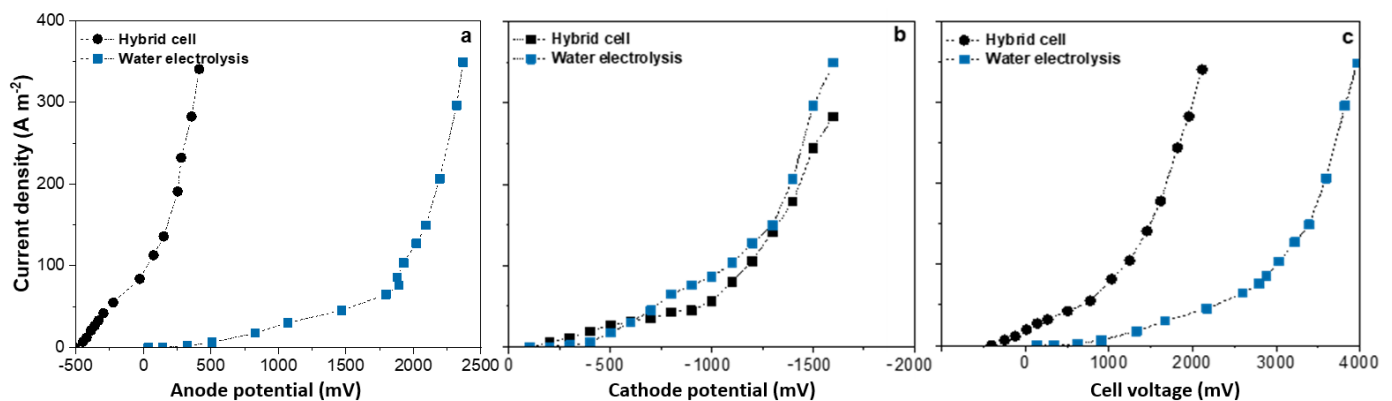


Figure 2. A comparison of polarisation performance (as a function of (a) anode potential; (b) cathode potential; and (c) cell voltage) between the alkaline water electrolyser and the hybrid cell.

The polarisation curve for water oxidation at a constant anolyte pH (~ 8) exhibited a high activation barrier (Figure 2a). The water oxidation reaction theoretically occurred at a potential of about +700 mV based on the Pourbaix diagram of water electrolysis, whereas the onset anodic potential was between +1500 and +2000 mV. This suggests an experimental overpotential between 800 and 1300 mV. After exceeding the water oxidation potential at about 2000 mV, the current increased linearly with the anodic potential.

The cathode polarisation curves appeared similar for both electrochemical cells (Figure 2b). The higher activation overpotential observed in the cathode polarisation curve compared to that in the anode polarisation curve is attributed to slower kinetics of the Volmer–Tafel mechanism of H_2 evolution reaction than that of H_2 oxidation reaction [38].

It is simple and convenient to evaluate the performance of two electrochemical setups by comparing the potentials (here named indicative potential) at low current densities after which a linear relationship between voltage and current signifies a constant resistance. The main factor affecting the overpotential at indicative voltage is activation polarisation, which dominates losses at low current densities, and the impact of ohmic losses resulting from cell parts and their configuration is insignificant. In the presented experiments, this indicative potential was observed at a current density of 100 A m^{-2} . In the alkaline water electrolyser, the indicative cell voltage required to achieve this current density of 100 A m^{-2} was about 3000 mV, whereas it was only 1200 mV for the hybrid cell. The additional voltage of 1800 mV needed for the alkaline water electrolyser comprises a 700 mV difference in theoretical anodic potentials between the OER in the alkaline water electrolysis cell and the HOR in the hybrid cell. Furthermore, there was an additional 1100 mV of overpotential.

At potentials higher than the indicative potential, both electrochemical cells showed a similar ohmic resistance of about 1.5 ohm.m^2 across the anion exchange membrane. This means using a gas phase anode in the hybrid cell did not have a prohibitive effect on the anion transport across the AEM.

3.2. Effect of H_2 Loading Rate on the Polarisation Performance of the Hybrid Cell

One of the most important technical aspects of the hybrid cell is the supplementation of sufficient H_2 at the catalytic surface area of the anode to satisfy load demand. To investigate the influence of the H_2 inflow rate on the polarisation curve, four hydrogen inflow rates were tested (Figure 3). By applying the Faraday calculation, the theoretical H_2 consumption rates corresponding to the current densities of 100, 200, and 300 A m^{-2} were about 1.5, 3, and 5 mL/min, respectively (considering the surface area of 25 cm^2). At a low H_2 inflow rate of 1.5 mL/min (equivalent to the theoretical current density of about 100 A m^{-2}), the anode showed a similar polarisation curve to the water oxidation reaction in Figure 2a at high current densities. This was attributable to fuel starvation on the anode side where the H_2 supply could not meet the theoretical H_2 demand. Thus, the HOR was substituted with the oxidation of accumulated water on the surface.

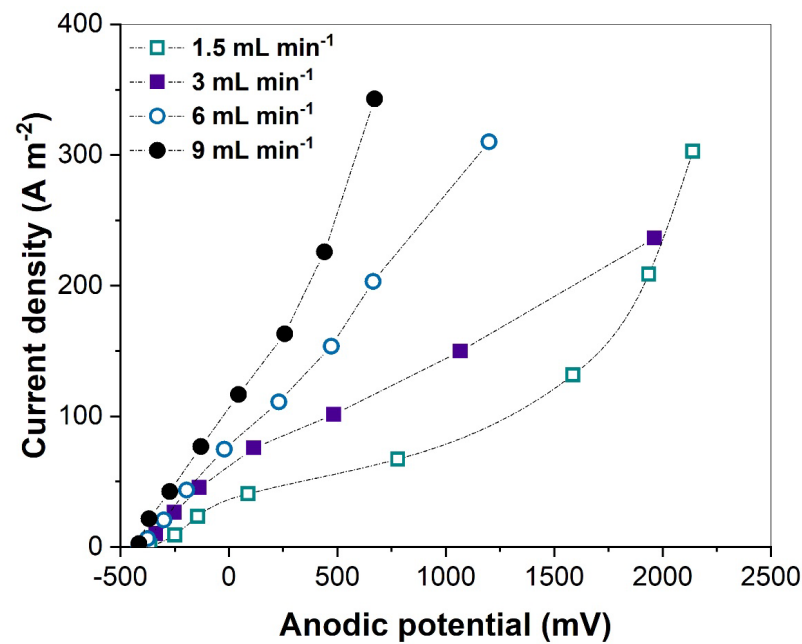


Figure 3. Anodic polarisation curve obtained at different H₂ inflow rates into the anode chamber.

With higher H₂ flow rates, the polarisation curve increasingly resembled that of the hybrid cell. A surplus hydrogen supply improved the polarisation performance of the hybrid cell by 30%. A similar trend was reported by Li et al. [39], who showed that the polarisation performance of the cell gradually increased with increasing H₂ flow rates to the anode. During the H₂ oxidation, the input H₂ was consumed at the anode, which caused the depletion of reactant near the electrode surface, hence the kinetic limitation. The higher H₂ inflow rate ensured a high hydrogen partial pressure in the anode chamber, which resulted in an increase in the drag force of convective diffusion from the diffusion layer to the catalyst layer to avoid gas transport losses [40,41].

3.3. H₂ Back Diffusion across the AEM

Any H₂ crossover through the AEM would decrease the efficiency of the hybrid cell. The H₂ gas permeated through the AEM owing to the partial pressure gradient. The rate of gas crossover through the membranes followed Fick's law, which is directly proportional to the diffusion coefficient and concentration gradient across the membrane and inversely related to the membrane thickness [42].

In order to measure the gas crossover rate through a dry AMI-7001 anion exchange membrane with a thickness of 0.45 mm, the H₂ gas content in the cathode compartment was recorded over time in the absence of an electric field, while H₂ gas was purged at atmospheric pressure on the other side of the membrane (Figure 4a). H₂ crossover current densities calculated from Faraday's laws of electrolysis in A/m² are shown in Figure 4b. The H₂ flux density was about 120 A/m² at maximum driving from across the membrane and decreased over time as the H₂ concentration on the permeate side increased, resulting in a reduction in the driving force for H₂ crossover. The H₂ crossover obtained in the present study was about three times higher than that measured for an AEM-based water electrolyser in Pushkareva et al. [43]. This could be attributable to the fact that the AEM employed in their measurement was hydrated, which diminished H₂ diffusion across the membrane. The diffusion coefficients of H₂ in water and air are 5.13×10^{-9} m²/s and 0.61×10^{-4} m²/s, respectively [44,45].

The H₂ permeability of the dry AMI-7001 was also calculated (Equation (12)). Dry AMI-7001 showed a high H₂ permeability of about 2500 barrer. Huang et al. [46] reported a similar H₂ gas permeability using dry QPIM-1 AEM, followed by an exponential decline when the membrane was hydrated. It is worth mentioning that H₂ flowed much slower

through the hydrated membrane than the dry one because the water molecule occupied the flow paths of the porous media.

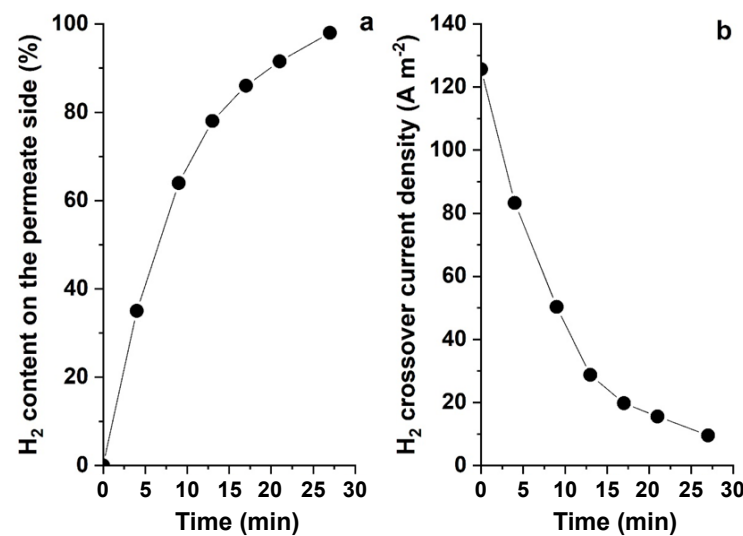


Figure 4. (a) H₂ gas concentration in the permeate side and (b) current density changes of a two-compartment cell due to gas crossover across the AEM (AMI-7001).

3.4. Faradaic Efficiency

Theoretically, the amount of H₂ consumed by the anode should follow Faraday's law, which is shown in Equation (10). During actual operation, however, possible leakage through sealing material and H₂ crossover through the AEM may reduce the Faraday efficiency. Nonetheless, the result showed that high Faraday efficiency of >90% was achieved with the tested system at high current densities (Figure 5). This suggests that the H₂ crossover through the hydrated AMI-7001 was insignificant at high current densities, as explained in Section 3.3. However, at lower current densities, the Faraday efficiency decreased to about 60%. Apparently, the effect of hydrogen gas leakage through the membrane or sealing material depends on the current density. Further study is required to verify this dependence.

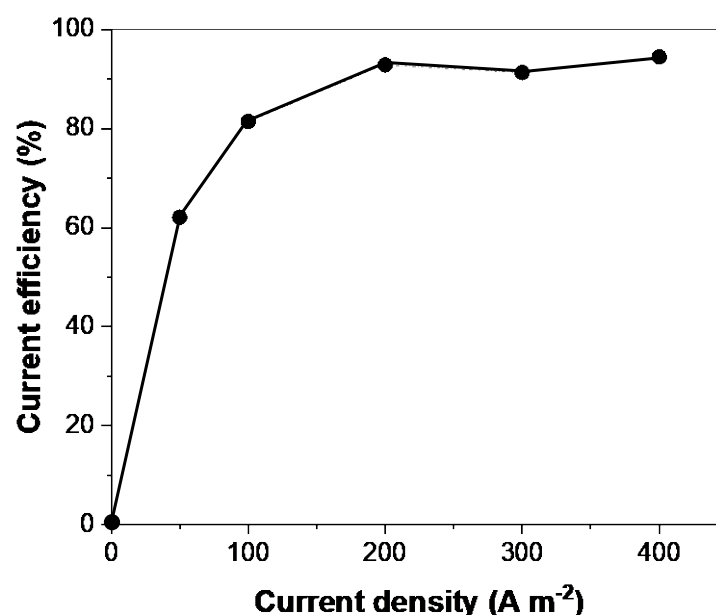


Figure 5. Effect of current density on current efficiency.

3.5. CO₂ Recovery Investigation

In electricity-driven CO₂ removal using an AEM-based electrochemical cell, the dissolved CO₂ in the catholyte, in the form of $\text{HCO}_3^-/\text{CO}_3^{2-}$, is transferred through an AEM to the anolyte, where it is stripped as CO₂ gas at low pHs. Previous work [35] has shown that in traditional O₂-forming electrolytic cells, a catholyte pH of nine enabled high-energy-efficient CO₂ transfer to the anode. In the current cell, CO₂ flux at pH 9 was maintained with 1M bicarbonate solution circulating from a tank to the cathode side of the cell. CO₂ flux across the AEM was determined by measuring the CO₂ emission from the anode (Figure 6a). The CO₂ flux across the AEM was proportional to the current density, indicating there was no concentration overpotential in the systems within the studied current densities.

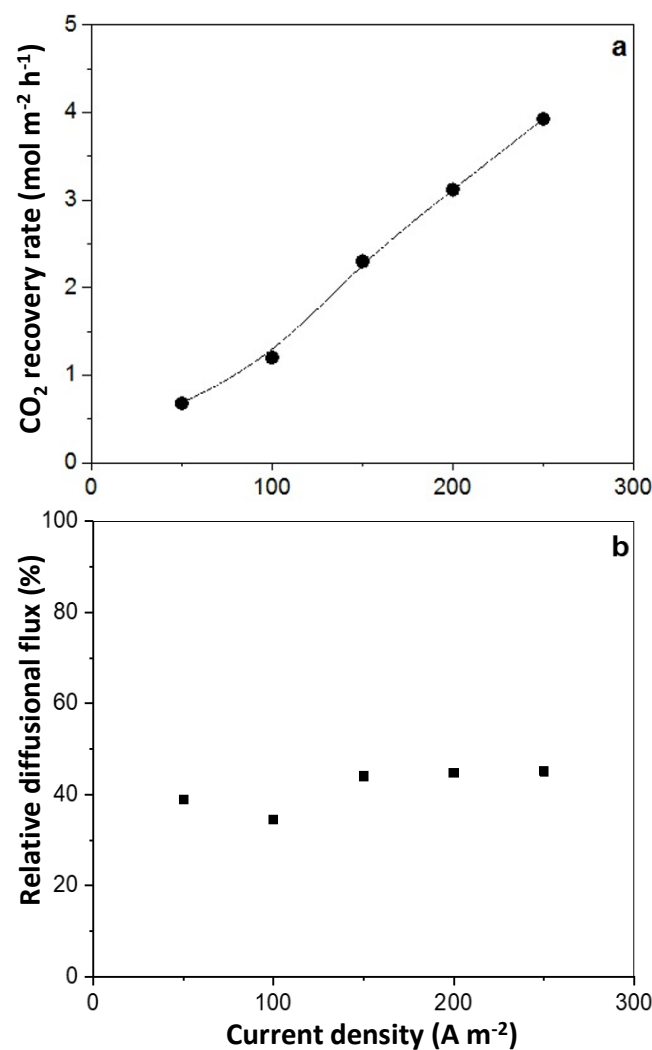


Figure 6. The CO₂ recovery rate from the permeate side (a) and relative diffusional flux, (b) as a function of the applied current density.

In the 1 M bicarbonate solution used as catholyte in this study, the main anion to act as a charge transferring species to transport the dissolved CO₂ at pH 9 is HCO_3^- . Hence, at a current efficiency of 100%, one Faraday of charges would theoretically transfer one mole of “CO₂” as HCO_3^- . However, the results showed that the measured dissolved CO₂ flux across the AEM accounted for only about 40% within the applied current densities (Figure 6b), which is similar to the findings reported for CO₂ separation from flue gas using an O₂ cycling electrochemical cell [24,47]. This relatively low efficiency proved that apart from bicarbonate, other anions participate in charge transfer across the AEM, or some

CO₂ gas diffuses back to the catholyte through the AEM. Hydroxyl and/or carbonate ions could contribute to some charge transfer. Considering the extremely alkaline medium near the membrane/electrode interface, where the H₂ generation reaction occurs, the concentrations of hydroxyl and carbonate ions could be dramatically higher than that in the bulk electrolyte, facilitating their migration across the AEM. Since carbonate requires twice as much the charge as required for bicarbonate, the migration of hydroxyl and/or carbonate ions was likely responsible for the loss of current efficiency. Another possible reason for this could be ion transport limitation across the ion exchange membrane, which violates the electroneutrality condition [48].

3.6. Energy Requirement Analysis

In this section, a simplified economic assessment is performed to compare the practical energy demand of conventional technologies for CO₂ removal from a gas mixture with newly developed electrochemical systems. The electrochemical systems for this separation process are classified into two categories: (i) redox cycling mode (H₂ cycling, O₂ cycling, quinone cycling, and copper ion cycling), and (ii) non-redox cycling mode (membrane electrolysis) (Table 1). The energy demand for CO₂ capture via electrochemical systems was estimated by considering both the cell voltage and the Faradaic efficiency (Equation (13)). The latter affects the operating current densities required for the process, whereby low current densities require larger equipment (electrode and membrane sizes). The energy content of H₂ (33.24 kWh/kg H₂) [49] was taken into account, and the generated H₂ was not recycled in the electrochemical cell. The CO₂ recovery rate was calculated based on the reported current densities, as the current density is directly related to the CO₂ recovery (Figure 6a).

A comparative study in this work showed that an H₂ cycling-based electrochemical cell is able to regenerate the spent alkaline solution for CO₂ capture with a minimum energy input of 0.19 kWh/kg CO₂ (equivalent to a cell potential of approximately 300 mV) at a CO₂ recovery rate of 0.7 mol/m²/h (equivalent to $I = 20$ A/m²), while it was about 0.31 kWh/kg CO₂ (equivalent to a cell potential of 1700 mV) for the water electrolysis device. Therefore, replacing the water electrolysis cell with the hybrid cell could save up to 30% of the energy input for electrochemical CO₂ capture within the CO₂ recovery rate in this work.

Other studies [25,34] also showed the energy expenditure of water electrolysis is higher than that of the electrochemical cycle systems, mainly due to sluggish four-electron transfer OER at the anode, which is an energy-intensive half-reaction [50]. The newly developed electrochemically mediated amine regeneration (EMAR) approach offers a competitive advantage over other electrochemically driven techniques. This technique is based on copper redox cycling, which requires a minimum energy of 0.22 kWh/kg CO₂ [51]. However, the amine-based absorbent employed in the EMAR technique causes some challenges related to corrosion and degradation [52]. Huang et al. [53] designed an energy-efficient electrochemical setup that was based on using quinone redox reactions to create a pH gradient for CO₂ capture. They employed a mixture of Tiron and NaOH solutions, termed Na₂Q, as an absorbent medium for CO₂ capture. However, the quinone reduction reaction is difficult to achieve at elevated catholyte pH values, which causes poor regeneration of alkaline absorbents.

Overall, the electrochemical CO₂ capture methods have often shown a minimum achievable energy demand of about 0.2 kWh/kg CO₂, which is considerably lower than the energy demand reported for the conventional chemical scrubbing technology (1.1 kWh/kg CO₂) [54]. However, the CO₂ recovery rate, which reflects the solvent regeneration rate, is considerably low at this energy requirement. At high CO₂ recovery rates, the energy requirement for electrochemically CO₂ separation is prohibitively expensive compared with the conventional CO₂ capture technologies such as chemical scrubbing due to low Faradaic efficiencies [54]. For example, to capture CO₂ from flue gas with a flow rate of 30–110 kg/h, and CO₂ partial pressure of 33–135 mbar (equivalent 90 to 140 mol CO₂/h) with a typical

electrochemical cell which constitutes of approximately 50 anodes and cathodes with a surface area of about 1 m² [55], a CO₂ recovery rate of about 3 mol/m²/h is required to regenerate the spent sorbent. At this CO₂ recovery, the electrochemically CO₂ capture exhibits a high operational energy requirement (about 2 kWh/kg CO₂).

Therefore, the electrochemical CO₂ capture process shows that it can be a competitive alternative to conventional technologies. However, the studied electrochemical designs have been operated at low CO₂ recovery rates, and optimisation for their performance at a high CO₂ recovery rate awaits future investigations.

Table 1. Summary of electrochemical CO₂ capture methods.

Cell Configuration	Mechanism	CO ₂ Sources	Faradaic Efficiency (%)	CO ₂ Recovery Rate (mol/m ² /h)	Energy Requirement (kWh/kg CO ₂)	Reference
Non-redox cycling mode	Water electrolysis	Biogas (55% CO ₂ , 45% CH ₄)	40	0.7–11	0.31–3.8	This study
	Water Electrolysis	Biogas (CH ₄ 60%, 40% CO ₂)	20–80	1.8–6	1.01–5.8	[25]
	Water Electrolysis	Aqueous carbonate/bicarbonate	10–100	0.37–7.4	0.63–5.6	[56]
Redox cycling mode	H ₂ cycling	Biogas (55% CO ₂ , 45% CH ₄)	40	0.7–11	0.19–2.8	This study
	H ₂ cycling	CO ₂ gas mixtures (50% CO ₂ , 50% N ₂)	80	1.8–3.7	0.18	[34]
	H ₂ cycling	Aqueous carbonate/bicarbonate	N.A	1.8–5.5	2.3–3.2	[57]
	O ₂ cycling	Flue gas	<25	0.37–1.8	0.48–0.73	[24]
	O ₂ cycling	Flue gas	45–65	0.07–0.7	0.8–1.1	[47]
	Copper ion cycling	Flue gas	45–60	0.4–0.7	0.22–0.31	[51]
	Quinone cycling	Flue gas	100	8.7	0.66	[53]

4. Conclusions

The technical and economic aspect of an electrochemical regeneration of spent alkaline solution for CO₂ capture was explored. The described hybrid cell using H₂ cycling provides a viable option to avoid the energy-intensive oxygen evolution reaction in the electrochemical regeneration of spent alkaline solutions for CO₂ capture. Our experimental results show that this approach could save up to 30% of the electrochemical work requirement for the regeneration of alkaline absorbent. In comparison with conventional regeneration techniques, electrochemical regeneration systems offer a low-cost opportunity for the deployment of CO₂ capture. Our assessment indicates that an advanced process modification is required, particularly for achieving high absorbent regeneration rates while maintaining a low energy requirement. Further, optimisation of the design and operation of the electrochemical cell such as mixing, electrodes, and the membrane is necessary to improve the energy efficiency of the process.

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Abbreviations

AEM	Anion exchange membrane.
OER	Oxygen evolution reaction.
HOR	Hydrogen oxidation reaction.
GDL	Gas diffusion layer.
EMAR	Electrochemically mediated amine regeneration.
F	Faradaic constant (96,485 A s/mol).
E	Net energy requirement (kWh/kg CO ₂).

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