Electrochemically Regenerated Solvent for Direct Air Capture with Co-Generation of Hydrogen at Bench Scale

primary project goal

The University of Kentucky Center for Applied Energy Research (UK CAER), Vanderbilt University, the Electric Power Research Institute (EPRI), and Louisville Gas and Electricity and Kentucky Utilities (LG&E and KU) are developing an intensified, cost-effective, and easily scalable process using aqueous potassium hydroxide (KOH) as a solvent for direct air capture (DAC). The process features the use of a hybrid membrane absorber (MA) coupled with an electrochemical solvent regenerator (ER) that is capable of extracting carbon dioxide (CO_2) from the atmosphere and pre-concentrating KOH solvent followed by regenerating the solvent to release CO_2 in the ER, and simultaneously refreshing the capture solvent while producing hydrogen (H_2) to offset the DAC cost.

technical goals

- Design and fabricate a hybrid bench-scale MA and ER with suitable electrode material and the flow channel pattern.
- Perform system integration, installation, and commissioning (EPRI and UK CAER).
- Pursue parametric studies of the bench-scale system through long-term operation, focusing on:
    1. Performance of the MA with a focus on CO_2 capture efficiency, gaseous pressure drop, and gas-liquid contact effectiveness (UK CAER and Vanderbilt).
    2. Performance of the ER with the target of minimizing both the operating voltage and H^+ transport through the cation-exchange membrane (UK CAER).
    3. Leveraging long-term operation to investigate the degradation mechanisms of both the electrode and membrane materials (UK CAER).
- Develop a techno-economic assessment (TEA) and life cycle analysis (LCA) to compare against commercial technologies (EPRI).

technical content

The two-unit operation employs a hybrid MA that extracts CO_2 from air, enriching carbon content in the solvent solution after capture, coupled with an ER that releases the CO_2 and simultaneously produces H_2 as a saleable byproduct. The process operates in a loop with a chemically stable and non-toxic potassium (K+) solvent that offers both fast absorption kinetics and near-zero vapor pressure. The system in Figure 1 shows: (1) a hybrid MA to capture CO_2 from the atmosphere to form carbonate (CO_3^{2-}), and (2) an ER to regenerate hydroxide (OH^-) while producing H_2 at the negative chamber.

program area:
Carbon Dioxide Removal

ending scale:
Bench Scale

application:
Direct Air Capture

key technology:
Novel Concepts

project focus:
Hybrid Membrane Absorber Coupled with Electrochemical Solvent Regenerator for DAC

participant:
University of Kentucky

project number:
FE0032125

predecessor projects:
N/A

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start date:
10.01.2021

percent complete:
10%

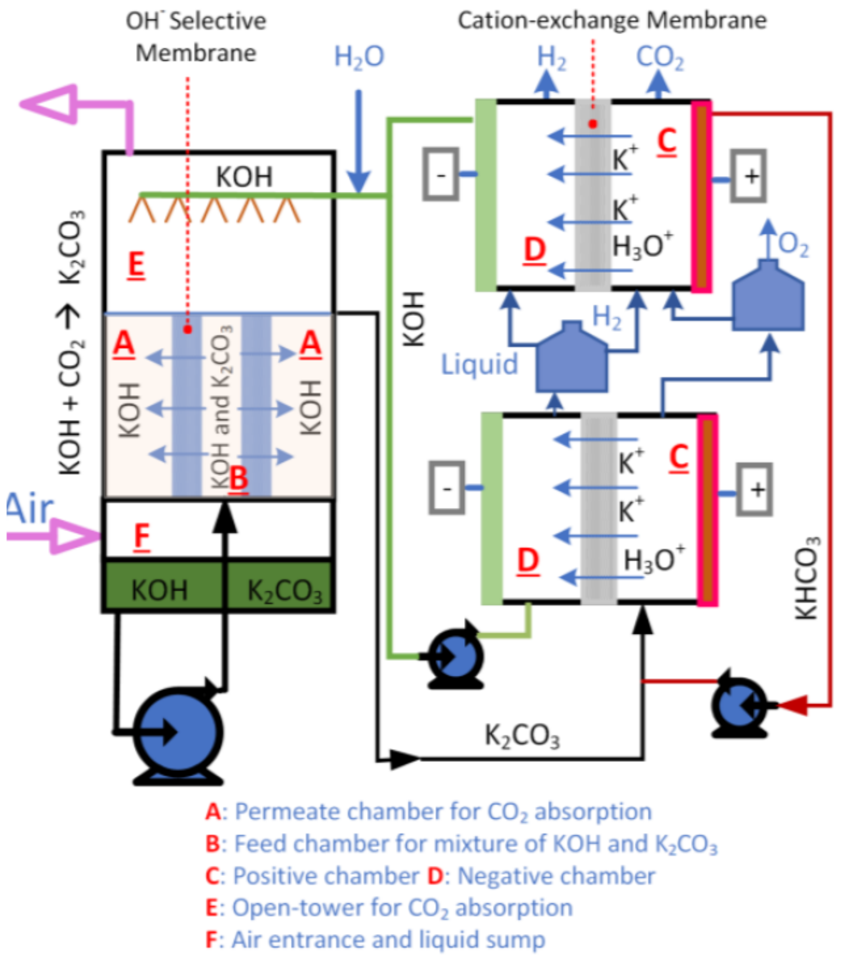

Figure 1: University of Kentucky Research Foundation (UKRF) solvent–based DAC process.

Key features of the process include: (1) utilizing dilute KOH as the capture solvent in a compact hybrid absorber; (2) using an OH^- selective nanofiltration membrane to concentrate carbon content in the rich solvent prior to regeneration to reduce the parasitic reactions; (3) producing saleable H_2 to offset the CO_2 capture cost; and (4) leveraging the mature technologies of nanofiltration and the alkaline electrolyzer to make the process easily scalable.

In addition to the solvent spray at the open tower (E) for CO_2 capture and air entrance above the liquid sump (F), the middle of MA has two chambers divided by an OH^- selective membrane acting as structured packing for gas-liquid contact, in which, at the permeate chamber (A) with large cross-section area (to maintain the gas velocity below 1.5 m/s) under ambient conditions, CO_2 from air is effectively captured using a 2~5 wt% KOH liquid. The majority of CO_2 is captured in the open tower section, while the wetted membrane surface provides the additional gas-liquid interface for reactions to boost the carbon loading. At the feed chamber (B) under a moderate operating pressure (e.g., less than 200 pounds per square inch gauge [psig]), K_2CO_3 collected from the prior CO_2 capture process from the sump is separated from the unreacted KOH. Furthermore, similar to a conventional alkaline electrolyzer, the ER is a compact electrochemical cell equipped with an ion-exchange membrane and catalytic positive and negative electrodes. At the chamber with the positive electrode, CO_2 gets liberated, and at the chamber with the negative electrode, H_2 gas is produced via typical water electrolysis.

As shown in Figure 1, the UK CAER process in brief, aqueous KOH produced from the negative chamber of the ER (D) enters the open tower of the MA from the top via liquid spray while air enters near the sump. Under such a countercurrent configuration, KOH reacts extensively with CO_2 from air to form K_2CO_3 via $2KOH + CO_2 = K_2CO_3 + H_2O$ under ambient pressure in the open tower, along with the permeated KOH in permeate chamber (A) flowing downward against the membrane surface. Subsequently, the unreacted KOH and K_2CO_3 are transferred from the sump to the feed chamber of the membrane, where the KOH gets selectively transported across the OH- selective membrane, leading to the purified CO_3^{2-} solution (e.g., K_2CO_3) prior to regeneration in the ER. The K_2CO_3 resulting from the MA is first pumped to the positive chamber (C) of the ER, in which CO_3^{2-} is converted to carbon dioxide (CO_2) via three-step reactions of 4OH- +

4e- = O_2 + $2H_2O$, CO_3^{2-} + H^+ = HCO_3^- followed by HCO_3^- + H^+ = CO_2 + H_2O. Meanwhile, K^+ is repulsed by electrostatic forces through the K^+ selective membrane to the negative chamber (D) to balance the electronic charge along with a portion of H^+. At the negative chamber with the liquid recirculation, H_2 is produced via $2H_2O$ + 2e- = H_2 + $2OH^-$ while forming KOH for the next CO_2 capture cycle in the MA. In the UK CAER process, the concentration of the K+-based solvent is adjustable with internal recirculation and make-up water (H_2O) to satisfy both the CO_2 capture performance in the MA and operating voltage for the ERs.

To produce a high-purity CO_2 stream, a two-stage ER is utilized in which two ERs with the same physical structure and functionality are connected in series. The bottom ER converts aqueous CO_3^{2-} to HCO_3^- and releases O_2 in the positive chamber. The HCO_3^- solution can then be flashed for CO_2 release or H_2 released in the negative chamber of the bottom ER is purged into the liquid fed to the positive chamber in the top ER, thereby biasing the positive electrode. Under such configuration, in the top ER, O_2 evolution at the positive chamber can be minimized via depolarization technique to facilitate the acidification process of $KHCO_3$ via HCO_3^- + H^+ = CO_2 + H_2O towards producing high-purity CO_2.

Process Features:

(1) Hybrid membrane absorber for CO_2 capture using diluted KOH solution. The low CO_2 concentration in air generates a significant challenge on the gas/liquid contact surface if a concentrated KOH solution is used. Compared to a liquid/gas mass ratio of 1 for the application of 5 M solvent to capture CO_2 from natural gas combustion flue gas (~4 vol% CO_2), applying the same solvent for air capture (~0.04 vol% CO_2) will result in the liquid/gas mass ratio as low as 0.01, which is too low to produce effective gas-liquid contact interface on any commercially available packing. One effective way to solve the challenge is to use the diluted solvent (e.g., 0.5–1 M). However, the lower the solvent concentration, the higher energy needed to regenerate the solvent after capturing CO_2. The hybrid MA (a) effectively absorbs CO_2 via spraying the solvent onto the mist in the open-tower, thereby reducing the overall capital cost of the absorber while enhancing CO_2 capture by hydroxide permeate on the membrane surface; and (b) reduces parasitic reactions by removing OH- and pre-concentrating the capture solution’s carbon content for the ER. The removal of OH^- prior to the solvent regeneration at the ER bottom eliminates the electron/charge transfer spent on the parasitic KOH neutralization toward non-CO_2 liberation at the positive chamber of the ER. For instance, when KOH enters the positive chamber of the ER, H+ reacts with OH- forming H_2O; in contrast, when K_2CO_3 enters the positive chamber of the ER, H+ reacts with CO_3^{2-} leading to the CO_2 product.

(2) Besides producing KOH as a highly effective CO_2 capture solvent, the ER can simultaneously generate ≥99.9% purity H_2 as a saleable carbon-free energy carrier, thereby offsetting the overall DAC process cost. In the proposed process, H_2 is produced at the negative chamber of the ER by accepting two electrons while liberating CO_2 at the positive chamber of the ER by giving away two electrons to produce H+, which means that for each mole of CO_2 captured from air, one mole of H_2 coproduct is produced through electrolysis. Furthermore, since H_2O is the only electrochemical active species at the negative chamber of the ER, 100% of electronic charge efficiency is expected toward H_2 production. In addition, internally recirculating the liquids help retain a high level of ionized species, therefore stabilizing the ER’s overall electrical conductivity. Such an operating configuration will further lead to H_2 production at a reliable operating voltage, thereby mitigating the voltage variation, which may be detrimental to the equipment lifespan.

(3) The proposed process is easily scalable to a larger scale, as both the MA and ER are built upon mature technologies. The MA is built upon liquid atomization and the nanofiltration technology, utilizing the membrane with either enhanced chemical surface charge or size-exclusion to selectively separate monovalent ions from divalent ions under a moderate operating pressure. For this case, OH- is separated from CO_3^{2-}. Moreover, the design of the MA will leverage the physical structure of the commercialized membrane contactors and spray towers, thereby providing a convenient pathway for modulation. The ER in the proposed process is slightly modified with respect to the conventional alkaline electrolyte. For this case, instead of using an anion-exchange membrane, a cation-exchange membrane is utilized to attain a high quality of KOH for efficient CO_2 capture from air while producing H_2.

In this project, the team is designing and fabricating a bench-scale unit (up to 10 cubic feet per minute air flowrate) and conducting parametric and long-term studies to inform next-scale process development.

TABLE 1: PROCESS PARAMETERS

Performance Attributes	Units	Current R&D Value	Target R&D Value
Carbonate Rejection/Hydroxide Rejection	%/%	50/<10	80/<10
Nanofiltration Membrane Fade	%/hr	N/A	0.02
ER K^+ Transport Efficiency	%	65	80
Membrane K^+ Transport Fade	%/hr	0.06	0.02
CO_2 Capture Efficiency	%	60	>90
Space Velocity	Hr^{-1}	1200	3600
Pressure Drop	Pa	N/A	1000
Regenerator Operating Potential	Volts	4	2.7
Regeneration Energy (55% thermal/electric)	kJ/mole	880	600
Overall Volumetric Productivity	gmol CO_2/ hr	0.001	2

Definitions:

Absorber Geometry – Hybrid absorber integrating nanofiltration stacking and liquid atomization in open tower architecture.

Atmospheric Air Feed-Gas Assumptions – Update values below to describe the air feed-gas pressure, temperature, and composition entering the capture system:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	68-72°F	0.04	variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

CO_2 Capture Mechanism – The driving force for capture is the partial pressure difference between CO_2 in air and the capture solvent on the nanofiltration face and in the open tower section. The electrochemical cell regenerates the solvent after CO_2 is absorbed to preserve the driving force.

Flue Gas Pretreatment Requirements – N/A

Product Streams Generated – Hydrogen for sale.

Process Design Concept – See Figure 1.

TABLE 2: DIRECT AIR CAPTURE ECONOMICS

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	\$/tonne CO_2	541	<200

Definitions:

Cost of Carbon Captured – The capture cost is estimated assuming ~4 V operation of the electrochemical regenerator, regenerator cost is >80% capture cost, 10 cents/kWh electricity cost.

technology advantages

- The proposed process is easily scalable to a large-scale, as both the MA and ER are built upon mature technologies.
- Simplified (two-unit operation) capture process with a significant reduction (greater than 25%) in both the capital and operating cost while producing H_2 as a saleable byproduct.
- Provide easy integration with renewable power sources for remote operation and reducing carbon emissions.

R&D challenges

- Design of anode-cathode to minimize voltage loss due to sluggish kinetics.
- Design of flow channel for rapid degassing.

status

UK CAER has begun designing and fabricating the CO_2 capture technology consisting of a hybrid MA that extracts CO_2 from air, enriching carbon content in the solution after capture, coupled with an ER for solvent regeneration. UK CAER is currently performing parametric evaluation for membrane integrity, transmembrane pressure, and OH^-/CO_3^{2-} selectivity for the MA, as well as cell development for the ER.

available reports/technical papers/presentations

Kunlei Liu, "Electrochemically Regenerated Solvent for Direct Air Capture with Cogeneration of Hydrogen at Bench-Scale," Project kickoff meeting presentation, November 20121. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12447&filename=Electrochemically+Regenerated+Solvent+for+Direct+Air+Capture+with+Cogeneration+of+Hydrogen+at+Bench-Scale.pdf*.