

Short communication

Reduction of CO₂ concentration in a zinc/air battery by absorption in a rotating packed bed

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Abstract

The reduction of CO₂ concentration in a gas stream containing 500 ppm of CO₂ by a technique combining chemical absorption with Hige (high gravity) was investigated in this study. Using a 2.0 L aqueous amine-based solution to treat the feed gas with a flow rate which varied from 12.9 to 20.6 L min⁻¹, piperazine (PZ) was found to be more effective than 2-(2-aminoethylamino) ethanol (AEEA) and monoethanolamine (MEA) for reducing the CO₂ concentration to a level below 20 ppm. The effects of temperature, rotating speed, amine solution flow rate, and gas flow rate on the removal efficiency of CO₂ were systematically examined. The results indicated that the proposed compact device could effectively reduce CO₂ to a level below 20 ppm, as required by a zinc/air battery, for a long period of time using PZ and its mixture with AEEA and MEA as the absorbents.

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1. Introduction

Due to the demand for energy saving, electric vehicles as a substitute for oil-burning vehicles have received widespread attention in recent years. Because a zinc/air battery has a theoretical specific energy (1084 Wh kg⁻¹) much higher than that of lead-acid battery (170 Wh kg⁻¹), MeH/NiOOH battery (217 Wh kg⁻¹), Li-ion battery (600 Wh kg⁻¹), and Na/S battery (765 Wh kg⁻¹) and uses ample and inexpensive materials such as zinc and air, it may be an ideal candidate for use in electric vehicles [1]. But if a zinc/air battery is used, CO₂ in the air would result in the formation of carbonate in the porous gas-diffusion electrode, causing a decrease in the performance and life of the battery. Obviously, the CO₂ concentration in the feed gases should be reduced.

Though some existing techniques such as chemical absorption [2–6], physical absorption [7,8], adsorption [9–12], and membrane [13,14] for removal of CO₂ from the exhausted gas streams of power generation plants exist, these techniques may not be applicable to remove CO₂ from the feed gas for a zinc/air

battery in vehicles due to the fact that the feed gas contains low CO₂ concentrations ranging from 300 to 900 ppm. To reduce the concentration of CO₂ in the air at a high flow rate to a level below 20 ppm, a very compact and efficient CO₂-scrubber needs to be developed.

Drillet et al. [15] used solid adsorbents including soda lime, LiOH, Ca(OH)₂, and a mixture of LiOH and Ca(OH)₂ to remove CO₂ from a feed gas containing 409 ppm of CO₂ at a flow rate of 50 L h⁻¹. The CO₂ concentration could be lowered to 20 ppm or less using 9.2 g of a LiOH–Ca(OH)₂ mixture. With this technique, solid expansion would occur on the formation of carbonate and the diffusion resistance for CO₂ would be increased. An alternative to achieving CO₂ removal is to use chemical absorption, a technique that has been widely used to treat the flue gases of power generation plants with high CO₂ concentrations. In these absorption processes, amine-based absorbents such as monoethanolamine (MEA), diethanolamine, methyldiethanolamine, 2-amino-2-methyl-1-propanol, PZ, AEEA, and their mixtures are commonly used [2–6,16–20]. But these processes require significant amounts of space for installation and operation. Further, those absorbents have not yet been verified as effective treatments for feed gas containing ppm levels of CO₂.

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Table 1
Physical and chemical properties of absorbents

	Absorbent		
	PZ	AEEA	MEA
MW	86.14	104.15	61.08
Density (293 K)	1.1	1.029	1.012
Boiling point (K)	420	513	443
Vapor pressure (293 K) (kPa)	0.1066	0.00015	0.0085
Vapor pressure (393 K) (kPa)	41.66	0.969	15.9
Solubility (293 K)	150 g L ⁻¹	Freely soluble	Freely soluble
Pseudo first order rate constant at 298 K (m ³ kmol ⁻¹ s ⁻¹)	53700 [2]	3717 [3]	3880 [26]
Activation energy (kJ mol ⁻¹)	35 [6]	N/A	46.7 [18]

It is known that significant mass transfer limitations exist in a packed absorber. To enhance the mass transfer rate between gas and liquid, a rotating doughnut-shaped packing device in which liquid and gas come into contact in the presence of a high centrifugal field may be employed as a substitute for the conventional packed bed. This technology has been denoted as Hige and was originally proposed by Ramshaw and Mallinson [21]. Lin et al. [22] and Tan and Chen [23] employed different aqueous amine solutions to capture CO₂ from a gas stream containing 10 mol% of CO₂ in a rotating packed bed (RPB). They observed better performance for RPB than that for a packed bed.

The objective of this study is to explore the feasibility of absorption in a RPB for the reduction of CO₂ concentration to a level below 20 ppm from a gas stream containing 500 ppm CO₂ that is fed to a zinc/air battery. To verify the applicability of the proposed CO₂ reduction technique, a high flow rate was employed. Since treatment was conducted on a gas with a low concentration of CO₂, amine-based absorbents with high reaction rate including PZ, AEEA, and MEA were chosen in

the study. Their properties are given in Table 1. The effects of temperature, rotating speed, solution flow rate, and feed gas flow rate on CO₂ reduction efficiency were examined. With each specific absorbent, the period of operation in which the CO₂ level could be maintained below 20 ppm was also examined.

2. Experimental

PZ, AEEA, and MEA with a purity of 99% were purchased from Acros Organics, Alfa Aesar, and Tedia, respectively. CO₂ with a purity of 99.5% and nitrogen with a purity of 99.99% were purchased from Boclh Industrial Gases. The amines and gases were all used as received. Fig. 1 illustrates the experimental apparatus in which CO₂ was absorbed by a circulated aqueous amine solution in a RPB. The inner and outer radii of the RPB were 7.6 and 16 cm, respectively, and the height was 2 cm. The total volume of the RPB was of 311.4 cm³ and could be fit to motorcycles and automobiles. The stainless wire mesh with a specific surface area of 803 m² m⁻³ and a void fraction

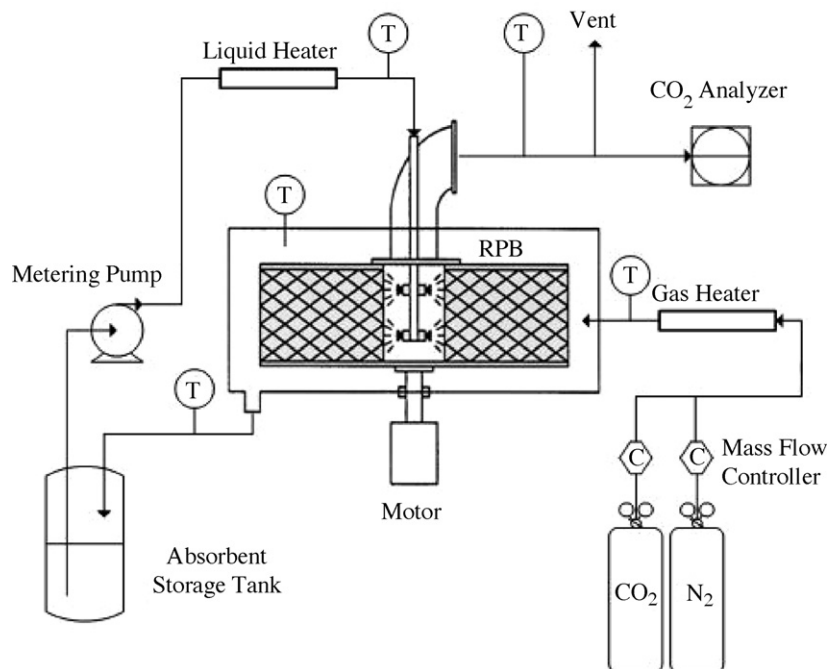


Fig. 1. Experimental apparatus for absorption of CO₂ in a rotating packed bed.

of 0.96 were packed in the bed and acted as the packing. The temperatures of the liquid and gas streams were heated by two heaters equipped with a temperature controller prior to entering the RPB.

The flow rates of CO₂ and N₂ gases were controlled by two mass flow controllers (Brooks Instruments, 5850E) to result in a CO₂ concentration of 500 ppm in the N₂ stream. The total gas flow rate was varied from 12.9 to 20.6 L min⁻¹. About 2.0 L of amine aqueous solution was prepared by adding a predetermined amount of individual or mixed amines into deionized water and was stored in a storage tank. In the circulation loop, a metering pump (Tacmina, PZD-32) was used to adjust and control the flow rate of the amine aqueous solution. The nitrogen gas stream containing CO₂ flowed inward from the outer edge of the RPB and the liquid absorbent was pumped from the storage tank to the inner edge of the RPB and left the outer edge via a centrifugal force. The discharged liquid solution flowed back to the storage tank. The flow rates of the liquid solution used in the study were observed to be high enough to avoid entrainment in the discharged gas stream. The CO₂ concentrations in the feed and discharged gas streams were measured by a NDIR CO₂ analyzer (Iijima Electronics Corp., LX-720). The reliable measurement range can be up to 2000 ppm with a resolution of 1.0 ppm.

3. Results and discussion

The reproducibility tests were performed for various combinations of operational variables. From the measured CO₂ concentrations in the discharged gas stream, it was observed that the time-dependent CO₂ concentrations could be reproduced with a deviation of less than 2%, indicating the measurement was reliable.

Fig. 2 shows that a rotating speed of 1000 rpm was better than that of 700 and 1300 rpm, though the difference was not so pronounced when 1.0 M PZ aqueous solution was used as the absorbent for the operation at 298 K, a liquid flow rate of 50 cm³ min⁻¹, and a gas flow rate of 18 L min⁻¹. When the rotating speed was varied from 700 to 1300 rpm, the corresponding

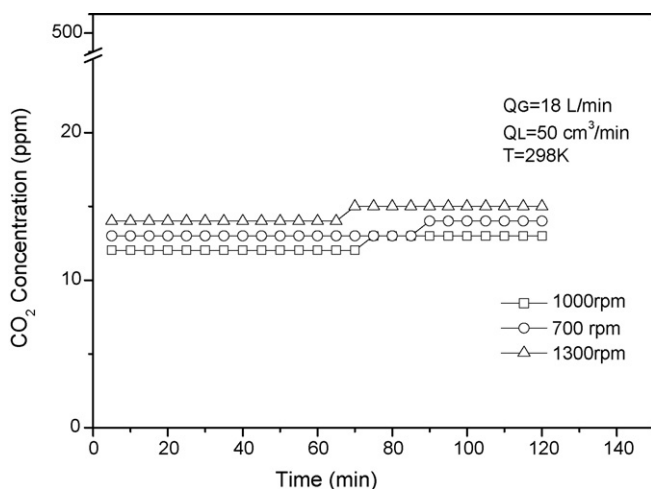


Fig. 2. CO₂ concentration in the discharged gas at different rotating speeds using 1.0 M PZ as the absorbent at 298 K.

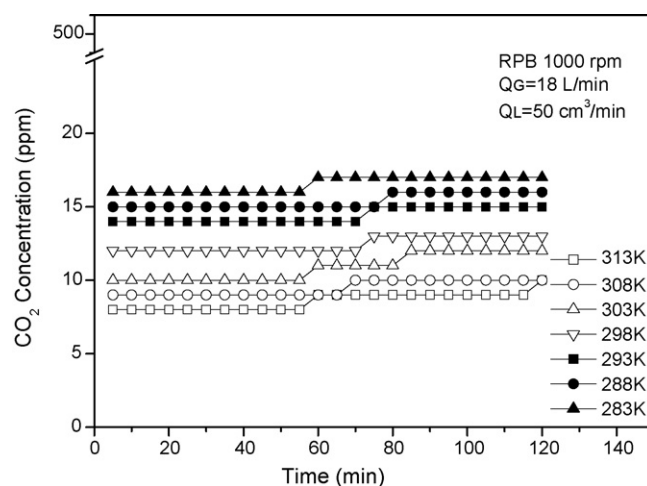


Fig. 3. CO₂ concentration in the discharged gas at different temperatures using 1.0 M PZ as the absorbent.

centrifugal acceleration was changed from 204 to 1483 m s⁻². A higher centrifugal acceleration would result in a higher mass transfer rate. This favors the absorption of CO₂. But the contact time, on the other hand, was reduced at high rotating speeds. That was unfavorable to absorption. A compromise therefore existed at an optimal rotating speed. Because 1000 rpm was found to be the best, this rotating speed was therefore fixed for the remaining studies.

When the CO₂ concentration in the feed gas was 500 ppm and the liquid and gas flow rates were fixed at 50 cm³ min⁻¹ and 18 L min⁻¹, respectively, Fig. 3 shows that the CO₂ concentration in the discharged gas stream at all the studied temperatures was less than 20 ppm for a period of 2 h, indicating that the 1.0 M PZ solution was a very effective absorbent for the removal of CO₂ from the feed gas. To take Phoenix in Arizona as an example, the average CO₂ concentration in the urban area is 390 ppm [24] which is lower than 500 ppm, the period of time in which CO₂ concentration is less than 20 ppm is therefore expected to last longer for treating a gas containing this average CO₂ concentration. It is also seen from Fig. 3 that more CO₂ could be removed from the feed gas at higher temperatures. It is supposed that the reaction rate constant follows the Arrhenius equation [2]:

$$k^{\infty} = k^0 \exp \left(-\frac{\Delta H_a}{R} \left(\frac{1}{T(K)} - \frac{1}{298.15} \right) \right)$$

where k^{∞} is the rate constant at a specific temperature, k^0 the rate constant at 298 K, ΔH_a the activation energy, and R is the gas constant. Obviously, a higher reaction rate occurs at higher temperatures. In this situation, more CO₂ could be removed from the feed gas at higher temperatures, as shown in Fig. 3.

Fig. 4 shows that PZ was the only absorbent to reduce the CO₂ concentration to a level below 20 ppm in 2 h of operation for aqueous solutions containing a single amine with a concentration of 1.0 M at 298 K. This was because PZ possesses the highest reaction rate with CO₂ as compared to AEEA and MEA, as indicated in Table 1. The contact time between gas and liquid in the RPB was much less than 1.0 s, as a consequence an amine

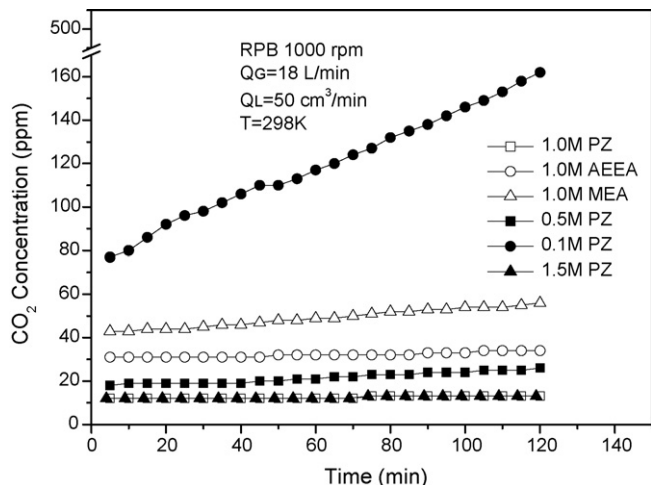


Fig. 4. CO₂ concentration in the discharged gas using individual amine as the absorbent at 298 K.

with a higher reaction rate with CO₂ should exhibit a higher CO₂ removal rate. It is also shown in Fig. 4 that the PZ concentration should be at least 0.5 M to make the CO₂ concentration less than 20 ppm; more PZ in solution favored CO₂ removal resulting from the fact that more PZ could participate in the reaction with CO₂ at higher concentrations. It is noted here that the 1.0 and 1.5 M PZ solutions corresponded to the solutions containing 8.6 and 14.4 wt.% of PZ, respectively. For a commercial process to remove CO₂ from the exhausted gases of power generation plants, the concentration of amines in aqueous solution varies from 20 to 50 wt.% depending on corrosion and vapor pressure of the amines used [25]. It is therefore expected that more CO₂ is removed from the feed gas when the PZ concentration is higher than 1.5 M. But due to the solubility limitation of PZ in water indicated in Table 1, PZ concentration in solution cannot be higher than 2.0 M at room temperature. To compensate for this limitation, PZ should be mixed with other amines to achieve a high amine concentration in solution if it is desired. Fig. 5 shows that a CO₂ level below 20 ppm could also be achieved using

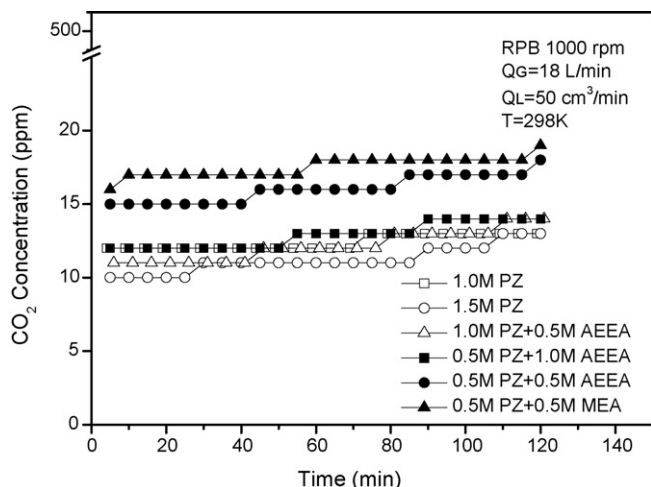


Fig. 5. CO₂ concentration in the discharged gas using mixed amines as the absorbents at 298 K.

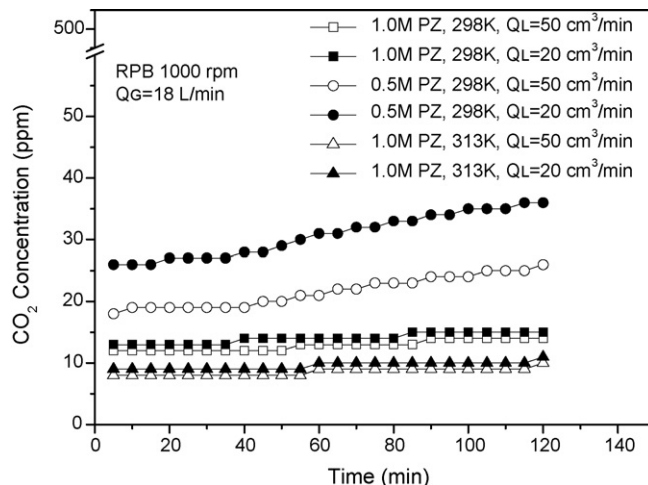


Fig. 6. CO₂ concentration in the discharged gas at different solution flow rates using PZ as the absorbent.

the 1.5 M mixed amine solutions containing at least 0.5 M PZ. Besides this, more CO₂ was found to be removed from the feed gas when more PZ was present in the mixture. It can also be seen from Fig. 5 that the CO₂ removal efficiency of a mixed amine could not be compared to that of a solution containing only PZ with the same total amine concentration, indicating that PZ was the most suitable absorbent for CO₂ removal. These results also indicated that absorption of CO₂ in a RPB was strongly affected by the reaction rate of the amine with CO₂. In this situation a proper choice of amine is essential to achieve a high removal rate of CO₂.

When the PZ solution flow rate was increased from 20 to 50 cm³ min⁻¹, the results in Fig. 6 show that the difference in CO₂ removal efficiency was not so significant for a PZ concentration equal to 1.0 M at 298 and 313 K, but this was not the case for the PZ concentration of 0.5 M at 298 K. As pointed out by Lin et al. [22], an increase in the liquid flow rate would reduce liquid-side mass transfer resistance and contact time. The former favors absorption but the latter exhibits the opposite effect. Besides this, a higher liquid flow rate would provide

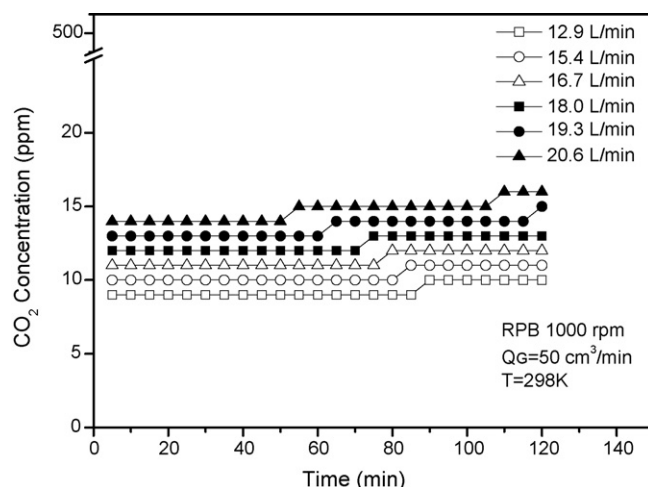


Fig. 7. CO₂ concentration in the discharged gas at different gas flow rates using 1.0 M PZ as the absorbent at 298 K.

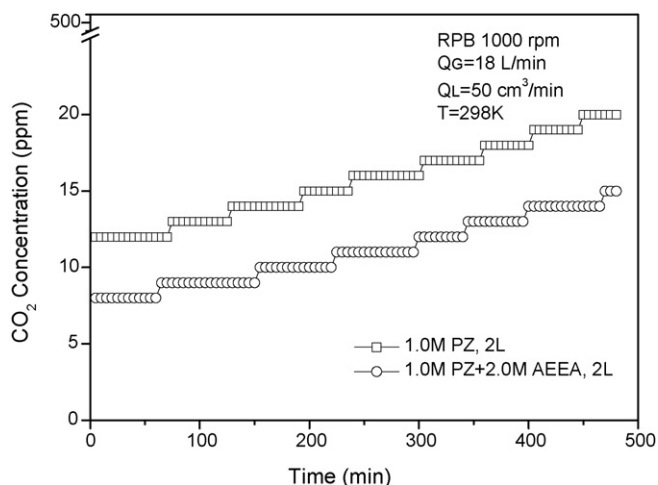


Fig. 8. CO₂ concentration in the discharged gas using 1.0 M PZ and a mixture of 1.0 M PZ + 2.0 M AEEA in a period of 8 h.

more absorbent to absorb CO₂, which might favorably affect absorption. The observed results for 0.5 M PZ solution at different solution flow rates therefore indicated that the PZ content was not high enough to achieve the CO₂ removal goal.

Fig. 7 illustrates CO₂ removal efficiencies at different gas flow rates using 1.0 M PZ solution as the absorbent at 298 K and a solution flow rate of 50 cm³ min⁻¹. Though all the CO₂ concentration levels could be less than 20 ppm in a gas flow rate range of 12.9–20.6 L min⁻¹, the CO₂ removal efficiency was found to be better at lower gas flow rates. An increase in gas flow rate would result in a reduction of gas-side mass transfer resistance if it exists. This would be beneficial to CO₂ absorption. But a reduction of contact time at a high gas flow rate would not provide enough time for the absorbent to absorb CO₂. From the obtained results, it was seen that the contact time exhibited an effect on CO₂ removal efficiency.

Fig. 8 shows that a CO₂ concentration level below 20 ppm could be achieved in an 8 h operation when the aqueous solutions with 1.0 M PZ and 1.0 M PZ + 2.0 M AEEA were used at a temperature of 298 K, a solution flow rate of 50 cm³ min⁻¹, and a gas flow rate of 18 L min⁻¹. Obviously, more CO₂ can be removed using a solution containing more PZ. From the results in Fig. 8, the applicability of the proposed device for the removal of CO₂ from the gas fed to a zinc/air battery is verified.

4. Conclusion

The reduction of CO₂ concentration to a level below 20 ppm from a feed gas containing 500 ppm CO₂ over a temperature range of 283–313 K and a gas flow rate range of 12.9–20.6 L min⁻¹ was achieved by absorption in a RPB using 2.0 L of amine-based aqueous solution. Though the experimental results indicated that a rotation speed of 1000 rpm was better than 700 and 1300 rpm, the effect of rotation speed on CO₂ removal efficiency was not so pronounced. The data obtained also indicate that the CO₂ removal efficiency could be adjusted by varying the amine concentration as well as the amine solution and gas flow rates.

From the measured CO₂ concentration in the discharged gas, PZ was found to be better than AEEA and MEA for removal of CO₂ from the feed gas. This was because PZ possesses the fastest reaction rate with CO₂. Due to the existence of a very short contact time between gas and liquid in a RPB, the results obtained therefore offered a criterion for selection of absorbent, which has a fast reaction rate with CO₂. While PZ was found to be very effective, a very high concentration in solution is not possible due to its solubility limitation in water. Besides this, a high loss of PZ in the regeneration stage may occur due to its high vapor pressure. A mixed absorbent compromising the advantages and disadvantages of individual amines is therefore suggested. A desired CO₂ concentration level in the feed gas was achieved using mixtures of PZ with AEEA and MEA. If there was a higher content of PZ in the mixture, a better removal efficiency could be achieved.

Because of the compact size of a RPB can fit in an electric vehicle and because of a long allowable operation time, the proposed device combining absorption with Higeer has great potential to be a CO₂-scrubber in an electric vehicle equipped with a zinc/air battery.

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