

Droplet microfluidic encapsulation of monoethanolamine and graphene nanoplatelet for high carbon capture performance

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ABSTRACT

Vigorous studies have been conducted for effective reduction of carbon dioxide (CO₂) and other greenhouse gases from anthropogenic sources as primary driver of climate change. Among a portfolio of technologies for CO₂ capture, storage and monitoring, microencapsulation of carbon solvents (MECS) has become promising and gained increasing attention in recent decade, as it can minimize the leakage of the solvent and enhance mass transfer with an increased surface area to volume ratio. In particular, encapsulation of carbon solvents via polymeric shells also circumvents the issues that carbon solvents normally encounter, such as high viscosity or corrosivity, by offering a protective layer between the solvents and absorption column. Although there has been recent progress towards microencapsulation of carbon solvents, the realization of which has focused mainly on use of polydimethylsiloxane (PDMS) devices which necessitate the use of clean room or glass capillary devices which are inherently difficult to align while fabrication. In this work, an off-shelf needle based microfluidic system has been established to form microcapsules with monoethanolamine (MEA) encapsulated in the silicone polymer shell made by TEGO RAD 2650 for carbon capture. The low-cost and facile method offers an exquisite control over the size, shape and inner structure of the microcapsules. MECS of MEA has higher absorption CO₂ rate than its neat solvent by at least a fold. Beyond that, incorporating graphene nanoplatelet (GNP) into the core solvent yields MECS of MEA with GNP, showing improved CO₂ uptake capacity by 10 and 60% when absorption was carried out

at 25 and 60°C, respectively. Therefore, the off-shelf droplet-based microfluidics opens up a new avenue for ease access to versatile fabrication of microencapsulated carbon sorbents with well-tailored properties in more cost-effective way, thus benefitting their pragmatic applications for carbon capture and utilization.

Keywords: microencapsulation, carbon dioxide absorption, graphene nanoplatelets, enhanced mass transfer, droplet microfluidics

NOMENCLATURE

A	Surface area, m ²
D	Diameter, m
H	Solubility coefficient
K	Mass transfer coefficient, m s ⁻¹
k	Reaction rate constant
l	Shell thickness, m
\dot{n}	Absorption rate, mol s ⁻¹
P	Pressure, Pa
Q	Volumetric flow rate, uL min ⁻¹
R	Universal gas constant, J mol ⁻¹ K ⁻¹
t	Time, s
T	Temperature, K
V	Volume, mL

Abbreviations

CNT	Carbon nanotubes
DEA	Diethanolamine
GNP	Graphene nanoplatelet
MEA	Monoethanolamine
MECS	Microencapsulated carbon solvents

PDMS Polydimethylsiloxane
 STC Shell-side mass transfer coefficient

Subscripts

exp Experimental
surf surface

1. INTRODUCTION

Microencapsulated carbon sorbent (MECS) are microscopic sorbents composed of thin layer of CO₂ permeable polymeric shell with a liquid core of reactive solutions. It is a new class of hybrid sorbent composed of liquid and solid materials, first devised and reported by the research team at Lawrence Livermore National Laboratory [1]. Carbonate solutions have first been investigated as potential core solvent for MECS, as they are abundant, environmentally benign, and resistant to degradation and have low volatility [2]. Such encapsulated sorbents enhance CO₂ absorption through an extended surface area for mass transfer and therein improves reaction kinetics for CO₂ absorption [3]. Immobilising the solvents within polymeric shells provides a protective layer to prevent the solvents from leakage. Microencapsulation has proven to enhance the absorption rate of encapsulated carbonate solvents along with few other anhydrous solvents. For example, encapsulating 30 wt.% sodium carbonate in MECS demonstrated CO₂ absorption rate of an order of magnitude higher relative to neat sorbents of equivalent mass when subjected to CO₂ exposure. Precipitation formed inside MECS was confirmed to be Nahcolite (NaHCO₃). The addition of CO₂ promoter – zinc (II) cyclen further increased the rate of CO₂ absorption [2]. These MECS appear to be both chemically and mechanically stable, and can be regenerated thermally. Fig. 1 shows the increment of absorption rates and specific surface area of microencapsulated carbon solvents in comparison to other solid sorbents [4]. The nominal capacity for existing carbon sorbents is typically in the range of 1-6 mmol CO₂ g⁻¹ at room temperature and atmospheric pressure.

Microencapsulation can be achieved using droplet microfluidics, which can be applied in a number of industrial and biomedical applications due to the versatile and precise control over the flow conditions and microdevice geometric configurations [5-7], as well as significantly enhanced heat and mass transfer effects [8-11]. One can see a spur of interest in using droplet microfluidics in recent years to generate the emulsions from single emulsion to double emulsion, and even

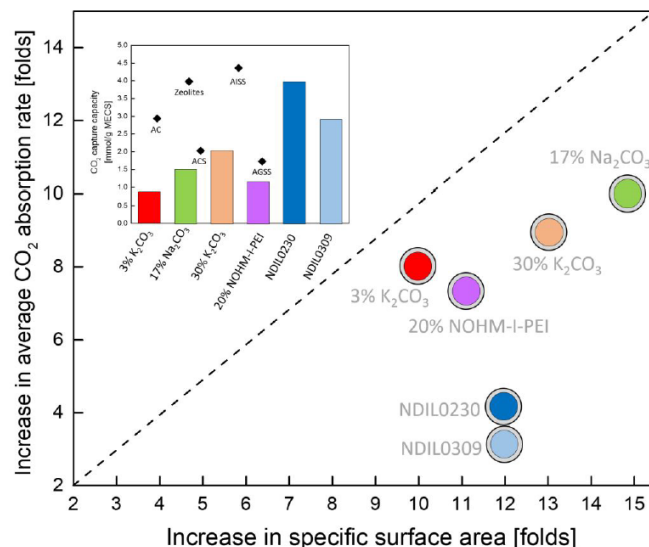


Fig. 1 A plot showing the enhancement in CO₂ capture capacity and increase in average CO₂ absorption rate of microencapsulated sorbents with core containing Ionic liquids (ILs), K₂CO₃, Na₂CO₃ and NOHM. CO₂ capture capacity range of solid sorbents such as active carbon (AC), zeolites, alkali carbonate sorbents (ACS), amine-impregnated solid sorbents (AISS), and amine grafted solid sorbents (AGSS) with the simulated flue gas (CO₂: 10-15 vol.%) is also presented [4].

higher order emulsions, and monodisperse particles and capsules at micro or nano-scale can be fabricated using the microfluidic platform [12-14]. Thereby microfluidics can lead to formation of the core/shell structured microcapsules with a high encapsulation efficacy. The volume ratio of the of the core and the shell can be precisely and independently varied using droplet microfluidic technology. The high monodispersity of microcapsule size distribution allows better control over mass transfer performance. Furthermore, droplet microfluidics technology works with various materials, including polymers, inorganic compounds, metal oxide and metal nanoparticles, hence droplet microfluidics enables accurate fabrication of MECS using double-emulsion droplet templates with a systematically varied size, structure, and composition for achieving tuneable mechanical and thermal properties as well as multifunctionality.

Herein, an off-shelf needle based microfluidic system is presented for the fabrication of MECS with tunable mass transfer performance for high carbon capture performance. Potassium carbonate, MEA, and MEA with GNP have been successfully encapsulated using water-in-oil-in-water (W/O/W) double emulsions. A fundamental understanding toward the stabilization of double-emulsion templates for robust formation of MECS with a uniform size, a well-controlled core-shell

structure, and tailored carbon capture capacity has been developed. It can be envisioned that droplet microfluidics would provide a versatile platform for precisely engineering high-quality MECS with desirable mass transfer properties to meet the demands of various carbon capture and utilization applications.

2. MATERIALS AND METHODS

2.1 Preparation of carbon solvents and nanofluids

As carbonate solutions have become the benchmark solvents for MECS technology, potassium carbonate (K_2CO_3) was thus used in parallel to evaluate the

Commercialised silicone polymer, TEGO RAD 2650 a product of Evonik with high CO_2 permeability of approximately 3,300 Barrer was chosen as the encapsulating material following material screening and compatibility test to ensure the microcapsules formed are stable [17]. Core-shell double emulsions with carbon solvents engulfed in silicone polymer were polymerised on-the-fly and cured rapidly upon exposure to UV irradiation. The MECS were kept in isotonic solutions to the capsule core to avoid excessive swelling and buckling prior to sorption tests due to diffusion of water into and out of the capsules shell as the shell layer is also highly permeable to water. MECS formed were 710 - 768 μm in

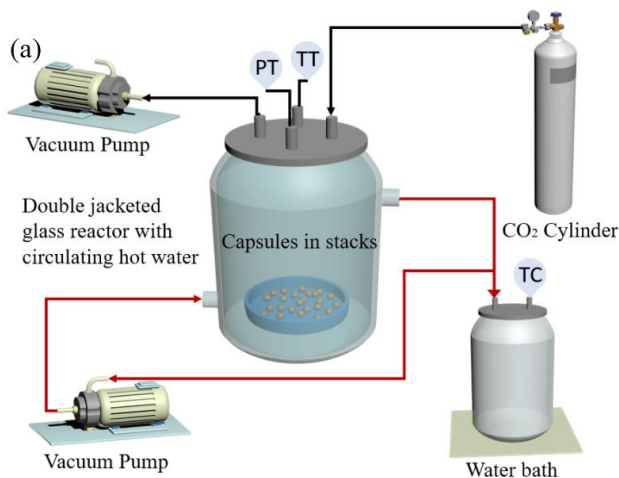


Fig. 2. (a) The schematic of the experimental setup for the measurement of CO_2 uptake of MECS in a constant-volume vessel. PT and TT are the pressure and temperature transmitters connected to a data logger, respectively, and TC is the temperature controller for water bath. (b) The photo of the experimental setup

absorption performance of MECS containing MEA. K_2CO_3 and MEA purchased from Sigma Aldrich were used as received to prepare 30 wt% of aqueous solutions. Nanofluid was prepared by adding 1 vol% of C300 graphene nanoplatelets from XG Sciences to aqueous MEA solution and the mixture was sonicated for 30 minutes to ensure good dispersion preventing GNP from agglomeration. Graphene nanoplatelets are nanoparticles consisting of short stacks of graphene sheets having a platelet shape. Graphene on its own is a CO_2 adsorbent that has garnered extensive research attention, mainly due to its excellent adsorption properties stemming from a high surface area [15].

2.2 Synthesis of double emulsions

Double emulsions containing aqueous K_2CO_3 , base MEA solution and nanofluids of MEA and GNP were synthesized via needle-based microdevice as demonstrated in previous work [16]. The ease of assembly of a facile needle device significantly reduces both cost and microfluidic device fabrication time.

size and shell thickness was approximately 60 - 75 μm .

2.3 Measurement of CO_2 uptake

The CO_2 uptake rate of MECS encapsulating three different solvents: K_2CO_3 , particle free MEA and MEA with nanoadditives, was determined volumetrically with a pressure-drop apparatus as described in the work of Hornbostel et al. [18]. The capsules were removed and rinsed with deionised water for several times and carefully dried. Thin layers of capsules were laid across stainless steel mesh and placed in a double jacketed glass reactor. The air inside the vessel was drawn and pure CO_2 was injected into the sealed vessel. The total pressure

and temperature in the sealed vessel were recorded every second for a period of an hour and subsequently used to determine the amount of CO₂ absorbed through the gradual change in pressure. A water bath was used for temperature control to maintain the temperature in the double jacketed reactor. Control tests with stagnant thin film (pool) about 1mm thick of both 30 wt.% K₂CO₃ and MEA solutions were also subjected to the pressure-drop test with the same setup as shown in Fig. 2.

2.4 Calculation of CO₂ uptake rate

The performance of MEA and K₂CO₃ MECS for CO₂ uptake were evaluated by subjecting the capsules to pure CO₂ in a constant volume vessel. The total pressure of the vessel was monitored over time and the pressure drop measurements were used to determine the absorption rate of CO₂, \dot{n}_{CO_2} (mol s⁻¹) across the MECS according to Eqs (1):

$$\dot{n}_{CO_2} = \frac{dP}{dt} \frac{V}{RT} \quad (1)$$

where volume, V of the vessel is 500mL, dP/dt is the cumulative pressure drop with time (Pa s⁻¹), R is the universal gas constant (J mol⁻¹K⁻¹) and T is the temperature expressed in Kelvin.

During gas absorption, CO₂ molecules are transferred from the bulk flue gas through the polymer membrane, and diffuses into the core solvent. The overall mass transfer coefficient which is a lumped parameter is indicative of the absorption performance in separation units, and is highly dependent on parameters such as effective surface area for absorption, reaction kinetics and thermodynamics of gas and solvent, as well as the hydrodynamics of the system [19]. The overall mass transfer coefficient, K_{exp} (m s⁻¹) for the capsules is determined based on experimental pressure drop via the following equation Eqs (2):

$$K_{exp} = \frac{\dot{n}_{CO_2} RT}{A_{surf} P_{CO_2}} \quad (2)$$

where A_{surf} refers to the total surface area for absorption and P_{CO_2} as the pressure of CO₂ in the vessel. The shell-side mass transfer coefficient, k_{shell} is expressed as in Eqs (3):

$$k_{shell} = \left(\frac{P_{CO_2}}{l} \right) RT \quad (3)$$

where \mathcal{P}_{CO_2} (Barrer, 1 Barrer = 3.348 × 10⁻¹⁶ mol m m⁻² s⁻¹ Pa⁻¹) is the permeability of shell material and l is shell thickness (m).

3. RESULTS AND DISCUSSION

3.1 Enhanced CO₂ uptake through encapsulation

The CO₂ absorption kinetics of both MEA and K₂CO₃ capsules were measured and compared against that of

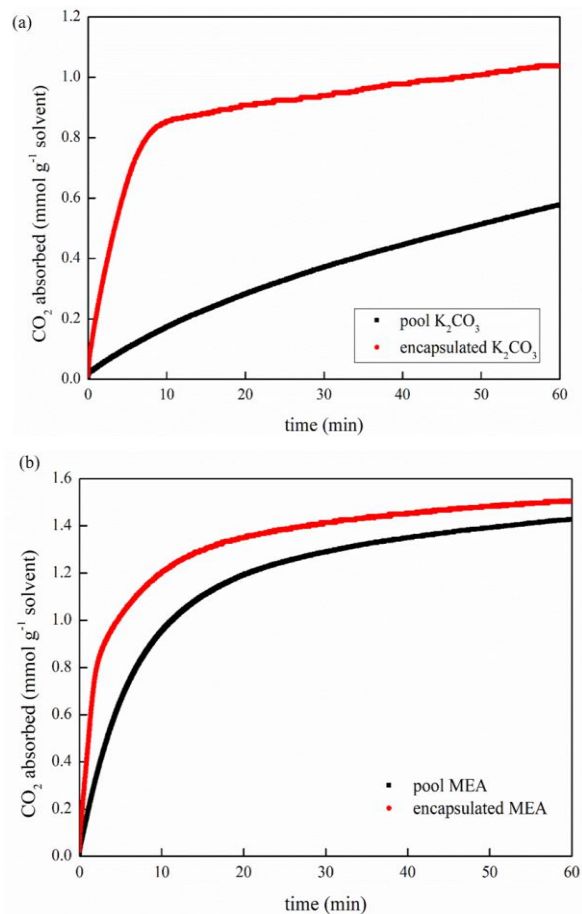


Fig. 3. Comparison of CO₂ uptake of encapsulated (a) K₂CO₃ and (b) MEA against their neat solvents as represented by a 1mm thick liquid film at 25°C.

their neat solvents at room temperature, and the results are shown in Fig. 3. According to Vericella et al. [2], a thin film of about 1mm thickness is a fair representation of the thickness of carbon solvent flowing down packings in a typical packed column. The total amount of CO₂ absorbed over time is normalized over mass of solvent. From Fig. 3, it is apparent that encapsulated K₂CO₃ achieved greater enhancement in CO₂ uptake by 5 to 6 fold, while despite an improved CO₂ uptake is achieved for encapsulated MEA, the enhancement is only approximately a fold.

Aqueous alkanolamines have been benchmark CO₂ capture solvents, especially aqueous ethanolamine (MEA) which is a primary amine that forms carbamate with CO₂ rapidly. In contrast potassium carbonate solution, despite having lower toxicity and tendency to degrade, has been limited by its slow absorption kinetics, in particular the hydration of CO₂ which is the rate limiting step. The extensive increase in surface area for CO₂ diffusion due to encapsulation is estimated to be about 12 times higher than that in packed columns [20], which sees a drastic increase in the uptake rate for

encapsulated carbonate solution. Even though MEA has intrinsically higher reaction kinetics, such vantage appears to be less prominent as the mass transfer of CO₂ into MEA capsules is then constrained by the shell side resistance as postulated by Yu et al. [4].

3.2 Encapsulated amine solution with nanoadditives

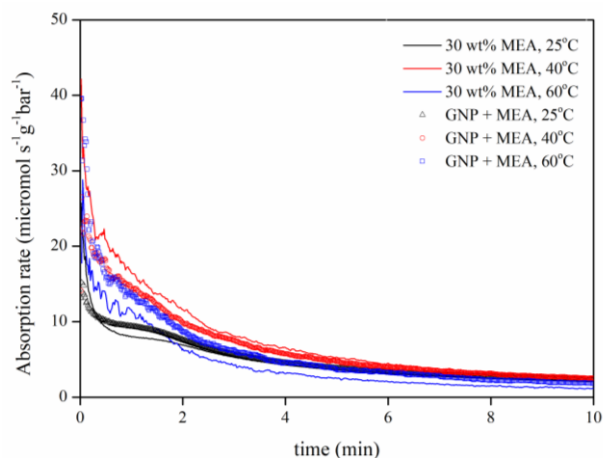


Fig. 4. Absorption rate of encapsulated MEA and MEA-GNP solvents at 25, 40 and 60°C.

The experiments were carried out at three different temperatures of 25, 40 and 60°C. The CO₂ uptake rates of base MEA and MEA-GNP capsules with temperature variance over the first ten minutes, normalised over total mass of MECS and partial pressure, are shown in Fig. 4. Generally the absorption rates increase with temperature for both MECS, and decrease progressively with time, as the solvents are gradually loaded with CO₂, even more so at higher temperature as water evaporates from the capsules. A drastic change in CO₂ uptake for encapsulated base MEA is noted at 60°C, as reflected in the rapid decline of uptake rate as well as the maximum CO₂ loading (mole CO₂ absorbed per mass water). This could be attributed to the dehydration of capsules at elevated temperature of 40 and 60°C, where the depletion of water in the MEA capsules adversely affect the diffusion and reaction of CO₂ with the basic solution. While the dissolution and absorption of CO₂ into carbon solvents are exothermic by nature, the effect of heat released during reaction was considered to be less significant as the rise in temperature was below 2°C when monitored real time.

An overall enhanced CO₂ uptake is observed with the incorporation of GNP in amine solution. The improvement of CO₂ uptake rate is more apparent at 25 and 60°C, while capsules with particle free base solvent performed better at 40°C. Such anomaly of reduced CO₂ loading rate was not expected for GNP containing solvent, and despite repetition of sorption tests, the

results remained the same. Notably, the maximum CO₂ capacity achievable for MECS with graphene increased by 60% from 0.021 gram CO₂ absorbed per gram MECS to 0.034 at 60°C, while a 10% increment was observed at 25°C in comparison with graphene free MEA MECS. This indicates that addition of GNP at 1 vol% has a favourable effect on stabilising mass transfer within MEA at 60°C in juxtaposition to that with GNP free solvent which recorded lowest CO₂ capacity attributed to loss of water. The highest recorded CO₂ capacities of K₂CO₃, MEA and MEA containing GNP MECS are 0.026, 0.037 and 0.040 g GO₂/g sorbent, which correspond well to the capacity of other known sorbents within 1 – 6 mmol GO₂ /g sorbent.

4. CONCLUSIONS

Despite the research is still at its infancy, MECS has presented itself as a promising solution to problems of existing carbon removal technologies such as high energy penalty and issues of physicochemical properties of new solvents that hinder the immediate employment in existing processes. This study enables a facile method using needle-based droplet microfluidics to form MECS for carbon capture applications. Our research also reveals that whilst micro-encapsulation would enhance the performance of carbon solvents, the type of solvents and the capsule shell thickness have significant impact on the CO₂ absorption rate. CO₂ capture performance for capsules containing aqueous MEA and potassium carbonate solutions has been evaluated and enhancement of up to 6 folds was recorded for capsules with K₂CO₃ while improvement of approximately 1-fold was observed for microcapsules encapsulating MEA solvent which is attributed to the shell resistance which becomes the limiting step for mass transfer of CO₂ in encapsulated solvents with fast reaction kinetics. An enhanced overall CO₂ uptake with a higher mass transfer coefficient was noted for MECS containing GNP in comparison with capsules with only base amine solution. Future study is needed to determine the optimum mass transfer enhancement that GNP-nanofluid and encapsulated nanofluids could benefit from, as well as to address the regeneration ability of the MECS.

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