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Immobilization of amino acid ionic liquids into nanoporous microspheres as robust sorbents for CO_2 capture†

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Xianfeng Wang,[ab] Novruz G. Akhmedov,[c] Yuhua Duan,[a] David Luebke[a] and Bingyun Li*[abd]

Supported nanoporous microspheres immobilized with amino acid ionic liquids (AAILs) as robust sorbents were developed for CO_2 capture. AAILs could be facilely immobilized into porous support materials. The developed sorbents exhibited fast kinetics as well as good sorption capacity, and can be regenerated and reused. The presented strategy may pave the way for developing AAIL-functionalized sorbents with high capacity and fast CO_2 transport kinetics.

Excessive CO_2 emission resulting from combustion of fossil fuel is a major anthropogenic factor in global warming.[1–4] One promising solution to reduce CO_2 emission from large emission sources (*e.g.* coal fired power plants) is to capture the generated CO_2 with sorbents before it is emitted in the atmosphere.[5,6] The predominant commercial CO_2 capture approach using aqueous amine scrubbing towards ammonium carbamate formation has some inherent disadvantages. These include relatively high amine loss and degradation, high energy consumption for regeneration, and unavoidable equipment corrosion.[3,7–9] Therefore, novel robust sorbent materials and technologies for efficient and economical CO_2 capture have attracted increasing attention from both academia and industry.

To overcome the above-mentioned drawbacks of aqueous amine solutions, ionic liquids (ILs) are considered to be attractive alternatives for the uptake of CO_2 because of their negligible vapor pressures, high thermal stability, and tunable physicochemical properties.[10–12] Many research groups, especially that of Brennecke,[13,14] have carried out significant research on the solubility of CO_2 in imidazolium-based ILs. In general, the absorption of CO_2 by these traditional ILs had to be performed under very high pressure and very long time for equilibrium to be reached,[15] which is not sufficient for practical CO_2 capture. Introduction of special groups to ILs to achieve more rapid and efficient absorption of CO_2 in ILs is possible.[5,12,16] Bates and co-workers developed a task-specific ionic liquid (TSIL) for CO_2 capture by introducing an amine group to the cation of ILs and found that the CO_2 uptake approached 0.5 mol mol^{-1} IL under normal pressure and temperature.[5] After that, a number of amine-functionalized ILs have been explored for CO_2 capture.[17–19] Among them, Fukumoto *et al.*[20] first reported the preparation of amino acid-based ILs (AAILs) from 20 natural amino acids in 2005. Since then, AAs have been used to act as a platform for the preparation of functionalized ILs and thus CO_2 sorbents or membranes.[12,15,21–26] For example, Zhang *et al.*[23] reported that (3-aminopropyl)tributylphosphonium amino acid salts ([aP_{4443}][AA]) could approach high CO_2 uptake within 80 min. Jiang *et al.*[12] have successfully synthesized tetraalkylammonium-based AAILs which presented improved reaction and mass transfer rates of CO_2 in the ILs.

Although the CO_2 absorption in AAILs is substantially improved, the relatively high viscosity of ILs results in low sorption and desorption rates and might limit their eventual use in large-scale CO_2 gas removal.[7,13,18,22] Immobilization of AAILs into porous inorganic supports is believed to be a promising strategy to prepare robust sorbents for CO_2 removal.[7] Herein, we conducted a proof-of-concept study showing that robust sorbents can be prepared through immobilization of 1-ethyl-3-methylimidazolium amino acid salts ([EMIM][AA]) into nanoporous polymethylmethacrylate (PMMA) microspheres. We developed supported AAIL sorbents with minimal CO_2 diffusion resistance and good capacity.

AAILs ([EMIM][glycine (Gly)], [EMIM][alanine (Ala)], and [EMIM][arginine (Arg)]) were prepared using a neutralization method reported previously.[20] In brief, the [EMIM][OH] solution prepared through anion exchange from the [EMIM][bromide (Br)] solution was added in slight excess of an equimolar AA (*i.e.*

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[a] *National Energy Technology Laboratory-Regional University Alliance (NETL-RUA), USA. E-mail: bili@hsc.wvu.edu*

[b] *Department of Orthopaedics, School of Medicine, West Virginia University, Morgantown, WV 26506, USA*

[c] *Department of Chemistry, West Virginia University, Morgantown, WV 26506, USA*

[d] *WVNano Initiative, Morgantown, WV 26506, USA*

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Gly, Ala, or Arg) aqueous solution to prepare [EMIM][AA] salts. After drying at 50 °C in a vacuum for 12 h, a crude product containing the desired AAIL and unreacted AA was obtained. Subsequently, ethanol was added to recrystallize and remove solvents. The mixture was then centrifuged to remove the insoluble AA, followed by vacuum drying, and [EMIM][AA] was obtained at an overall yield of ~75% (Scheme 1). All of the resulting three AAILs obtained were transparent, light yellow liquids at room temperature (Fig. S1†), and had a significant weight loss around 200 °C (Fig. S2†) due to thermal decomposition.

We next investigated the CO_2 uptake behaviors of [EMIM]-[AA] solvents (Fig. S3†). The liquid [EMIM][AA] was spread in a thermogravimetric analysis (TGA) microbalance quartz sample cell, heated to 105 °C in the N_2 atmosphere and then adjusted to 40 °C to measure the CO_2 uptake. As illustrated in Fig. S3,† the sorption rate of liquid [EMIM][AA] (~35 mg) was very slow due to the high CO_2 diffusion resistance caused by the high viscosity of ILs. The capacity of the three liquid [EMIM][AA]s (~35 mg) was less than 0.2 mmol g^{-1} within 45 min. When the amount of [EMIM][AA] placed in the TGA sample cell was reduced to 7 mg, which allowed [EMIM][AA] to be effectively spread in the sample cell, the sorption rate was significantly enhanced and reached a sorption capacity of 0.47, 0.45, and 0.09 mmol CO_2 per g solvent within 45 min for [EMIM][Gly], [EMIM][Ala], and [EMIM][Arg], respectively. The CO_2 uptake by [EMIM][Gly] and [EMIM][Ala] AAIL (Table S1†) was comparable to those of standard sequestering amines such as monoethanolamine (MEA) and diisopropanolamine (DIPA).[5]

To enhance the sorption rate, adsorption of CO_2 by supported [EMIM][AA] in nanoporous PMMA microspheres, prepared using the impregnation–vaporization method,[6,27,28] was studied. Fig. 1 presents the typical scanning electron microscopy (SEM) images of as-prepared [EMIM][AA]–PMMA sorbents, indicating that the resultant sorbents had a uniform diameter of about 500 μm. The high-magnification SEM image (Fig. 1b) clearly shows that the surface of the PMMA microsphere featured a hierarchical roughness and nanotexture. By closely observing the cross-section of the sorbents (Fig. 1c), it can be seen that the interior of the microspheres retained a highly porous structure (Fig. 1d). These observations led us to conclude that the versatile nanoporous structure of [EMIM][AA]-based sorbents can facilitate the diffusion of gas into and out of the microspheres, which may be very useful for applications as CO_2 sorbents.[29] This idea was confirmed by the CO_2 capture performance, as shown in Fig. 2. The resultant [EMIM][AA]–PMMA sorbents could overcome the high viscosities of the [EMIM][AA]s such that the resultant sorbents exhibited a dramatically enhanced sorption rate (CO_2 adsorption equilibriums could be reached in less than 15 min) due to the high mass transfer area of AAILs after immobilization. When exposed to CO_2, the adsorption capacity of [EMIM][Arg], [EMIM][Ala], and [EMIM][Gly] was 1.01, 1.38, and 1.53 mmol CO_2 per g sorbent, respectively (Fig. 2). The [EMIM][Gly]-based sorbents achieved the best CO_2 capture performance. It was generally believed that a CO_2 adsorption capacity of >1 mmol CO_2 per g sorbent may potentially reduce the cost of CO_2 sequestration.[30] The CO_2 adsorption capacity of our solid sorbents is comparable to newly developed sorbents like silica-supported tetraethylenepentamine[31] and activated carbon-supported tertiary amidine,[32] which had capacities of 2.1 and 0.86 mmol CO_2 per g

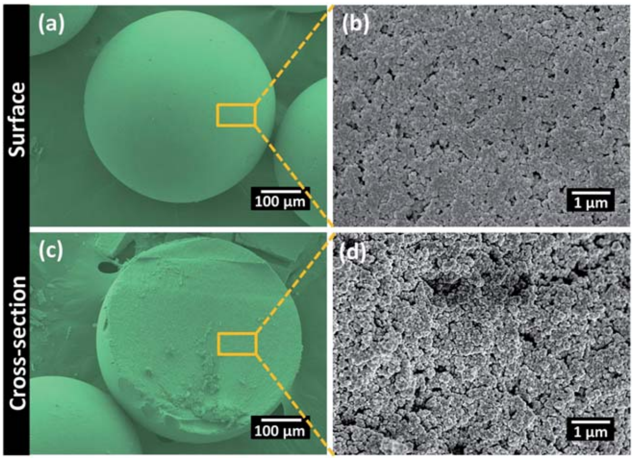
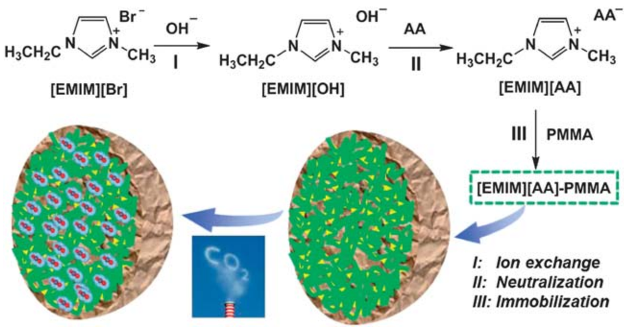


Fig. 1 Typical SEM images of as-prepared [EMIM][AA]–PMMA sorbents. (a and b) Surface structures; (c and d) cross-section structures.



Scheme 1 Schematic diagram of synthesis and immobilization of functional [EMIM][AA] for CO_2 capture.

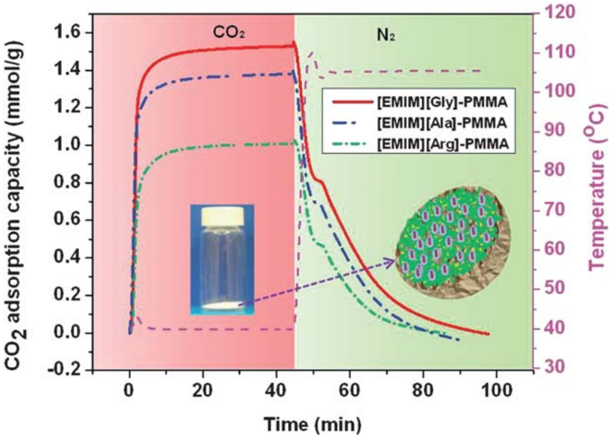
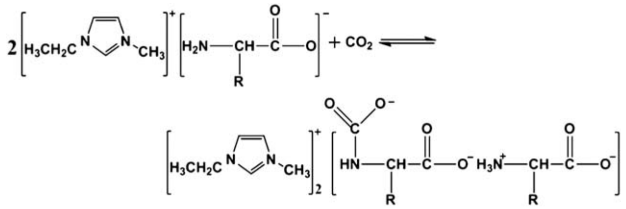


Fig. 2 CO_2 adsorption/desorption of three different sorbents [EMIM][AA]–PMMA (with an [EMIM][AA] loading of 50 wt% in the sorbents). The inset shows the photo-image of as-prepared [EMIM][AA]–PMMA sorbents.

sorbent, respectively. In addition, the process of CO_2 uptake in our AAIL sorbents is reversible and [EMIM][AA]-based sorbents could be regenerated by exposing them to flowing N_2 at 105 °C for 60 min (Fig. 2), indicating their practical use as solid sorbents for CO_2 removal. It is worth noting that the desorption was fast in the beginning but slow toward the end, similar to the phenomenon reported in other sorbents.[6,10]

The enhanced sorption properties of [EMIM][AA]–PMMA sorbents led us to explore their CO_2 sorption mechanism. For amino-functionalized TSILs, both 1 : 1 and 1 : 2 reaction stoichiometry mechanisms were proposed.[10] Gurkan *et al.*[11] argued that anion-functionalized ILs (*i.e.* trihexyl(tetradecyl)phosphonium amino acid or $[P_{66614}]$[AA]) can react with CO_2 in a 1 : 1 stoichiometry, *i.e.* only forming carbamic acid but not carbamate. The 1 : 1 stoichiometry theory works with $[P_{66614}]$[AA] ILs but fails in other anion-functionalized ILs (*e.g.* tetraethylammonium amino acid or $[N_{2222}]$[AA],[12] tetrabutylphosphonium amino acid or $[P(C_4)_4]$[AA][33] and 1-*n*-butyl-3-methylimidazolium amino acid or $[C_4MIM]$[AA][24]). For ILs with large-sized ion pairs (*e.g.* $[P_{66614}]$[AA]), it is difficult for two amino groups to approach each other so that only carbamic acid is formed according to 1 : 1 stoichiometry.[10] When the ion pair size of ILs is small, the formed carbamic acid can approach and further react with another amino group to form a neutral carbamate in 1 : 2 stoichiometry.[10,15] The capture mechanism of CO_2 in our developed [EMIM][AA] solvents and sorbents is believed to be similar to that of $[C_4MIM]$[AA],[24] *i.e.* one CO_2 molecule interacts with two amino groups (1 : 2 stoichiometry):



The experimental CO_2 sorption capacities of [EMIM][Gly] and [EMIM][Ala] approached 0.5 mol mol^{-1} AAIL, their theoretical maximum value for CO_2 capture (Table S1†). It is noteworthy that the experimental CO_2 sorption capacity of [EMIM][Arg] presents an obvious discrepancy with its theoretical value (Table S1†); the reason behind this is still unknown.

To determine the effect of [EMIM][AA] loading in sorbents on CO_2 capture performance, [EMIM][Gly] with various loadings (*i.e.* 0, 20, 40, 50, 60, and 100 wt%) was immobilized into the PMMA particles (Fig. S4 and S5†), and their CO_2 capture performance was determined using the TGA method (Fig. 3). When the [EMIM][Gly] loading was 0 (*i.e.* PMMA particles), the capacity was 0.5 mmol g^{-1}, which was attributed to physical adsorption. The capacities of PMMA sorbents with [EMIM][Gly] loadings of 20, 40, 50, 60, and 100 wt% were 0.82, 1.36, 1.53, 0.62, and 0.47 mmol per g sorbent, respectively. It could be seen that the capacity increased with increasing [EMIM][Gly] loading until 50 wt% loading followed by a decrease in capacity (Fig. 3, inset). At 60 wt% loading, the large amount of [EMIM][Gly] could have blocked some of the pores of PMMA particles (Fig. S5†) and thus reduced the accessible specific surface area of the sorbents leading to reduced capacity. The CO_2 adsorption of [EMIM][Arg]–PMMA sorbents with various [EMIM][Arg] loadings, shown in Fig. S6,† exhibited similar trends.

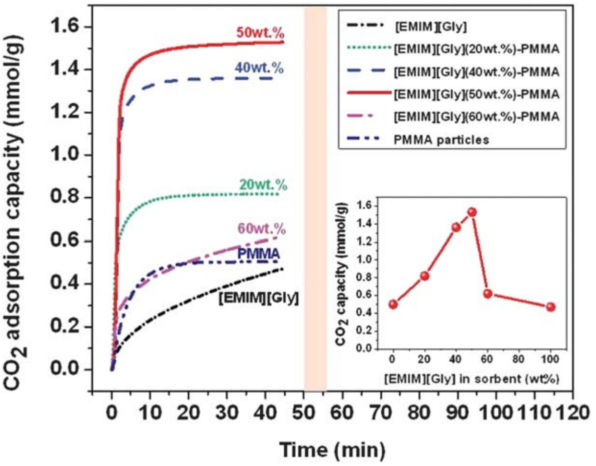


Fig. 3 CO_2 adsorption of [EMIM][Gly]–PMMA sorbents with various [EMIM][Gly] loadings (0 or PMMA, 20, 40, 50, 60, and 100 wt% or [EMIM][Gly]) in the sorbents at 40 °C. The inset shows the CO_2 capacity *vs.* [EMIM][Gly] loading in sorbents.

Fig. 4 presents the effects of sorption temperature on CO_2 uptake properties. It can be seen that the CO_2 capture capacity decreased almost linearly with increasing temperature, with the highest (1.71 mmol per g sorbent) and lowest capacities (1.02 mmol per g sorbent) at sorption temperatures of 25 and 80 °C, respectively. This is because the interaction between a sorbent and a sorbate is weakened as the temperature increases. It is noteworthy to point out that our [EMIM][Gly]-based sorbents possess higher capacity (Fig. 4) at 80 °C than that (0.86 mmol per g sorbent) of activated carbon-supported tertiary amidine sorbents at 29 °C.[32] The estimated activation energy of CO_2 adsorption in [EMIM][Gly] (50 wt%)–PMMA sorbent was approximately 6.8 kJ mol^{-1}.

Multiple cycle tests of [EMIM][Gly]–PMMA sorbents were conducted and are presented in Fig. 5. No obvious changes of adsorption rate were observed. A small decrease in adsorption capacity was seen and might be attributed to a possible incomplete desorption during regeneration. The adsorption and desorption operations were completed in 40 and 60 min, respectively, and about 1.5 mmol CO_2 was captured per gram sorbent in each cycle. Fourier transform infrared spectroscopy (FTIR) experiments showed no obvious chemical degradation in [EMIM][Gly]–PMMA sorbents during multiple cycles (Fig. S7†).

In summary, three [EMIM][AA]-type AAILs were synthesized and immobilized into nanoporous PMMA microspheres for CO_2 removal. The developed AAILs could be facilely immobilized into nanoporous microparticles with various loadings. More significantly, the sorbents retained the highly porous structures after AAIL loading and exhibited fast kinetics as well as reasonably high sorption capacity and could be easily regenerated and reused. When exposed to CO_2 at 40 °C, [EMIM][Gly]–PMMA sorbents achieved the highest CO_2 capture capacity [1.53 mmol per g sorbent or 0.49 mol mol^{-1} AAIL] compared with the other two sorbents, following the 1 : 2 stoichiometry

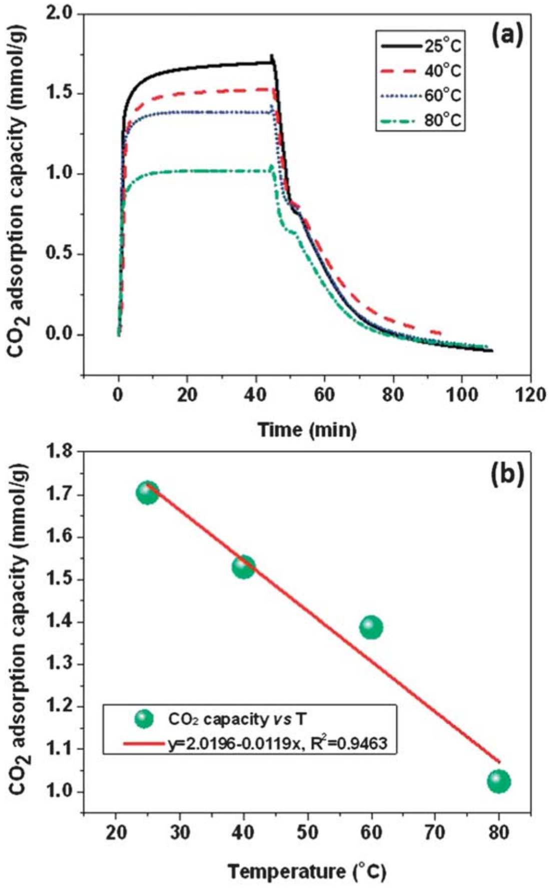


Fig. 4 (a) CO_2 sorption of [EMIM][Gly] (50 wt%)–PMMA sorbents at 25, 40, 60, and 80 °C. Desorption progress was conducted by flowing N_2 at 105 °C for 60 min. (b) CO_2 capacity *vs.* temperature.

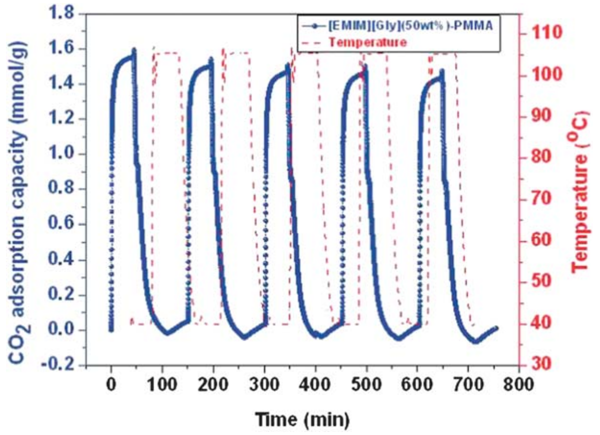


Fig. 5 Cycles of CO_2 adsorption/desorption into/out of [EMIM][Gly] (50 wt%)–PMMA. Each cycle consisted of flowing CO_2 at 40 °C for 45 min and then flowing N_2 at 105 °C for 60 min.

theory. In addition, the CO_2 uptake performance of the resultant sorbents indicated that the adsorption properties of AAIL sorbents could be finely tuned *via* sorbent structure, AAIL loading, and sorption temperature. The presented pathway may pave the way for developing similar AAIL functionalized sorbents with high capacity and fast CO_2 transport kinetics.

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