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Solid-State Poly(ionic liquid) Gels for Simultaneous CO₂ Adsorption and Electrochemical Reduction

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Abstract

Managing carbon dioxide (CO₂) released from large-scale industrial processes is of great importance, yet there remain significant technical challenges. Herein, the fabrication of 1- mm-thick solid-state electrochemical devices based on poly- (ionic liquid) ionogels with embedded electrodes capable of both adsorption and electrochemical reduction of CO₂ is reported. The ionogels are prepared via radical polymerization and chemical crosslinking of a vinyl imidazolium trifluoromethanesulfonimide ionic liquid monomer in the presence of additional ionic liquids (ILs) that act as swelling agents and enhance ionic conductivity. The effects of the ILs concentration and the degree of crosslinking on the mechanical properties, conductivity, and CO₂ adsorption of the ionogels are investigated. The ionogels are shown to have ionic conductivities as high as 0.6 mS cm⁻¹. The results of quartz crystal microbalance analyses demonstrates that the CO₂ adsorption of the ionogels reaches up to 22 mg g⁻¹, which is 10-fold higher than that of their native ionic liquid. Moreover, the ionogels are easily recoverable after CO₂ adsorption. The flexibility, conductivity, and CO₂ capture capacity of this system can be controlled by the crosslinking ratio and ionic liquid content of the ionogels. This electrochemical device has the potential to be used in large scale plants for capturing CO₂ for further electrochemical reactions.

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Solid-State Poly(ionic liquid) Gels for Simultaneous CO₂ Adsorption and Electrochemical Reduction

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Managing carbon dioxide (CO₂) released from large-scale industrial processes is of great importance, yet there remain significant technical challenges. Herein, the fabrication of 1-mm-thick solid-state electrochemical devices based on poly(ionic liquid) ionogels with embedded electrodes capable of both adsorption and electrochemical reduction of CO₂ is reported. The ionogels are prepared via radical polymerization and chemical crosslinking of a vinyl imidazolium trifluoromethanesulfonimide ionic liquid monomer in the presence of additional ionic liquids (ILs) that act as swelling agents and enhance ionic conductivity. The effects of the ILs concentration and the degree of crosslinking on the mechanical prop-

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Introduction

Carbon dioxide (CO₂) is the primary greenhouse gas and its emission has continuously increased because of the extensive use of fossil fuels, thereby causing unpredictable changes in the environment. While many industries are looking for alternative sources of energy to lower CO₂ emissions, it is also rational to capture and utilize this gas for other value-added purposes. The post-combustion gases released by power plants account for 40% of the total CO₂ emission, and currently there are only a few methods for CO₂ capture and utilization.^[1]

The selectivity, high adsorption capacity, and ability to regenerate the adsorbed gas are desirable properties that need to be considered when designing a system for capturing CO₂.^[2] Currently, aqueous solutions of amines, such as monoethanolamine, are used on a commercial scale for CO₂ capture from natural gas production industries. However, the shortcomings of these systems include the high cost of the process due to the high heat capacity of water,^[3,4] excessive pressure-induced loss of absorbent, the corrosive properties of the materials, and thermal degradation. Solid adsorbents have been used as alternatives to solve some of the problems associated with aqueous alkanolamine solutions.^[5] Metal organic frameworks (MOFs),^[6,7] zeolites,^[8] and polymers with CO₂-adsorbing functional groups are examples of the solid adsorbents that have been proposed for CO₂ capture.^[9] However, while CO₂ capture by MOFs and zeolites can range from ≈ 0.5 to 400 mg g⁻¹ at 1 bar and 273 K, it is difficult to utilize these systems on a large scale because of their brittleness and cumbersome processing.

Recently, ionic liquids (ILs) have been highlighted as promising materials for their capacity to selectively absorb 1 to 2 mg g⁻¹ CO₂ at 1 bar.^[10–13] ILs exhibit high thermal and chemical stability,^[14–17] and can be easily incorporated into solid substrates such as porous silica to develop solid adsorbents with improved performance due to their higher surface area.^[18–21] However, these systems can only operate at low pressures in order to prevent IL loss during the recovery and separation process.^[22] Poly(ionic liquids) (PILs), polymers derived from monomers based on ILs, have also been investigated for CO₂ capturing.^[23–26] PILs are ionically conductive and their CO₂ adsorption capacity is between 2 and 20 mg g⁻¹, which is higher than their IL counterparts.^[2,27–31]

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In addition to passive CO₂ capture, it is useful to convert the adsorbed gas to valuable reagents. As an example, Zhang et al. used a sulfonate-based MOF with embedded Lewis acidic sites to produce cyclic carbonates through the reaction of epoxides and the captured CO₂. The conversion yield of cyclic carbonate products was between 40% and 99%.^[32] Other catalysts such as ferroporphyrin, copper nanocrystals, transient metal oxides, and palladium have also been used for the conversion of CO₂ into other valuable products and feedstocks via electrochemical reduction.^[33–36]

In this study, we have developed a new strategy in which a solid electrolyte system is designed for simultaneous CO₂ adsorption and its electrochemical reduction. To this end, we synthesized ionically conductive gels, acting as solid-state electrolytes that are also capable of CO₂ adsorption. The ionogels are based on a crosslinked PIL network and an ionic liquid swelling agent, namely 1-ethyl-3-methylimidazolium trifluoromethylsulfonimide (EMI.TFSI), which is added to the network to enhance the conductivity of the system for electrochemical reactions. By adjusting the IL content and the crosslinking ratio of the ionogels, we are able to control the relevant properties to achieve the desired mechanical stability, ionic conductivity, and CO₂ adsorption capacity.

Results and Discussion

Synthesis of PIL gels

The full details of the synthesis of reactive monomers and the preparation of the ionogels are provided in the Experimental Section and schematically presented in Scheme 1.

Scheme 1. Synthesis of EVI.TFSI monomer (2).

Briefly, an intermediate IL monomer (**1**, Scheme 1) was prepared from the reaction of 1-vinylimidazole and bromoethane, which was subjected to an ion exchange process to obtain the final 1-ethyl-3-vinylimidazolium trifluoromethanesulfonimide (EVI.TFSI) monomer (**2**, Scheme 1).

PIL ionogels were then prepared via the radical polymerization of the EVI.TFSI monomer in the presence of the crosslinking agent and EMI.TFSI. The latter was used as a swelling agent for the PIL ionogels. As shown in Table 1, nine different compositions of ionogels were synthesized and the effects of IL content and the crosslinking ratio on the mechanical properties, ionic conductivity, and CO₂ adsorption of the ionogels were examined. Various solid structures were fabricated from these ionogels because of their robust mechanical properties (Figure 1). As an example, Figure 1b demonstrates the formation of a hollow and flexible tubular structure from ionogel IGX₁₀IL₃₀₀. Such tubular structures could be used in large scale plants for capturing CO₂ in exhaust pipes.

Figure 1. a) An example of a cylindrical POIL gel and b) a hollow tube made of POIL gel infused in cotton. Scale bars are 2 mm in (a) and 5 mm in (b).

Mechanical properties of PIL gels

The stiffness of the prepared PIL gels was measured using indentation testing.^[37] In Figure 2, the Young's moduli of the PIL gels are presented as a function of the amount of EMI.TFSI swelling agent in the ionogels (Figure 2a) and the degree of crosslinking (Figure 2b). The crosslinked PIL network with no EMI.TFSI had a Young's modulus of 90.7±21.8 kPa. The PIL network swollen in EMI.TFSI, on the other hand, exhibited a considerable decrease in Young's modulus, with the stiffness continuing to drop as the amount of EMI.TFSI in the ionogel was increased (Figure 2a). At 40% EMI.TFSI in the ionogel, the Young's modulus decreased dramatically to 12.3±3.1 kPa. In the ionogel network swollen with EMI.TFSI, the IL molecules acted as a diluent, hence decreasing the mechanical resistance of the network against external forces. In a swollen elastomeric network, the diluting effect of the swelling agent on the mechanical stiffness of the network can be summarized by Equation (1):^[38]

$$E \propto Q^{-1/3} \quad (1)$$

Table 1. Composition of monomer solutions. The amounts of EVI.TFSI monomer and initiator were constant in all formulations at 450 mg and 25 mg, respectively.

	Sample code ^[b]								
	IGX ₁₀ IL ₀	IGX ₁₀ IL ₁₀₀	IGX ₁₀ IL ₁₅₀	IGX ₁₀ IL ₂₀₀	IGX ₁₀ IL ₂₃₀	IGX ₁₀ IL ₃₀₀	IGX _{7.5} IL ₃₀₀	IGX ₅ IL ₃₀₀	IGX _{2.5} IL ₃₀₀
DMF, ^[a] [mg]	450	350	300	250	220	150	150	150	150
EMI.TFSI, ^[a] [mg]	0	100	150	200	230	300	300	300	300
BIS, ^[a] [mg]	10	10	10	10	10	10	7.5	5	2.5

[a] DMF: dimethylformamide, EMI.TFSI: 1-ethyl-3-methylimidazolium trifluoromethylsulfonimide, BIS: *N,N'*-methylenebis(acrylamide). [b] In IGX_iIL_j, *i* and *j* indicate the amount of, respectively, BIS crosslinking agent and EMI.TFSI in the formulation in mg.

Figure 2. a) Stiffness of ionogels as a function of IL molar ratio and b) crosslinking agent molar ratio. IL, M, and CL refer to EMI.TFSI IL, EVI.TFSI monomer, and BIS crosslinking agent, respectively.

where E is the Young's modulus of the swollen network and Q is the volumetric swelling ratio. The results in Figure 2a show that the Young's modulus of PIL gels is linearly proportional to the inverse of the cubic root of the swelling ratio of the gels, suggesting that the EMI.TFSI was purely a diluting factor in the network. It is important to note that the Young's modulus of an unswollen PIL network did not fit with this trend due to the fact that at ambient conditions the PIL polymer chains in the unswollen network depart from the elastomeric state towards the glassy state. The glass transition temperature (T_g) of the pure PIL based on EVI.TFSI monomers was 110 °C, which is significantly higher than the ambient temperature at which the mechanical testing was conducted. The T_g of ionogels varied with the amount of EMI.TFSI in their network, clearly following the rule of mixture (Supporting Information). The observation of a single T_g for ionogels suggests that the interaction between PIL and EMI.TFSI is merely physical mixing with EMI.TFSI having a plasticizing effect.

The data in Figure 2b demonstrate a correlation between the degree of crosslinking and the Young's modulus of the ionogels, where the modulus continuously increases with crosslinking ratio. The Young's modulus increased from 2.65 kPa to 12.25 kPa when the degree of crosslinking was raised from 1.4 mol % to 5.6 mol %. The increase in Young's modulus was inversely proportional to the molecular weight

between two adjacent crosslinking points (i.e., M_c^{-1}) as depicted in Figure 2b and Equation (2):^[38]

$$E \propto M_c^{-1} \quad (2)$$

Equation (2) is valid for an ideal elastomeric network, which suggests that the mechanical behavior of the ionogels resembles an elastomeric network.

Conductivity of PIL gels

A critical aspect of these ionogels is their ionic conductivity, which can be utilized for the development of PIL gels in functional devices. The ionic conductivity of the PIL gels was measured using a two-electrode set-up. Figure 3 shows that the ionic conductivity of PIL gels was a function of the degree of crosslinking and ionic composition of the ionogels, as both these factors impact the mobility of the ionic species. The ionic conductivity was elevated by increasing the IL content and also by decreasing the degree of crosslinking. The impact of the IL content was more paramount than the crosslinking ratio: the conductivity was increased 15 fold when the IL content was increased by a factor of two, while it was elevated only 2.6 fold when the crosslinking ratio was

Figure 3. a) Conductivity of ionogels as a function of IL molar ratio and b) crosslinking agent molar ratio. Arrows indicate the same sample. IL, M, and CL refer to EMI.TFSI, EVI.TFSI monomer, and BIS crosslinking agent, respectively. The error bars are smaller than the size of the data points.

reduced by 4.3 fold. The addition of IL reduces the T_g of the network and increases the chain mobility as well as the relative number of mobile ionic species within the gel. Both these factors enhance mobility of ions and increase the ionic conductivity of the network. Similarly, reducing the crosslinking ratio increases the chain mobility and facilitates the mobility of the ionic species, which results in higher ionic conductivity.

CO₂ capture

The effects of IL content and of the degree of crosslinking on the CO₂ adsorption of the PIL gels were studied using quartz crystal microbalance with dissipation monitoring (QCM-D) and thermogravimetric analysis (TGA). For QCM tests, thin films of ionogels with different composition were deposited over the quartz sensors. Then, the changes in frequency and dissipation at different overtones ranging from 3 to 11 were measured during the passage of N₂, CO₂, or under vacuum inside the QCM flow chamber. No frequency or dissipation change was observed during the passage of N₂, meaning that the PIL gels did not adsorb N₂ gas. However, during the passage of CO₂, the frequency decreased and dissipation increased for all ionogel compositions (Figure 4 a).

The fact that the changes observed in the dissipation (D) were larger than those observed for the frequency (f) and

within different harmonics means that the viscoelastic properties of the films were a function of CO₂ adsorption. Therefore, the mass change due to gas adsorption cannot be directly derived from the frequency change using the Sauerbrey equation (see Experimental Section). The f and D changes measured for different harmonics were then fitted using the Kelvin–Voigt model to obtain the mass changes. The calculated mass change (Δm) as a function of time (t) was fitted using the pseudo first-order adsorption Equation (3) to obtain the mass of adsorbed CO₂ at equilibrium (q_e):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

The pseudo-first order equation is used to describe those systems in which the sorption process is non-reactive.^[39] The process of CO₂ adsorption by imidazolium ILs is most likely physical and non-reactive.^[40] All Δm versus t curves were fitted to a linear correlation ($R^2 = 0.99$). The calculated CO₂ adsorptions at equilibrium normalized to the mass of ionogel, q_e , are presented in Figure 4b, as a function of the amount of IL in the ionogels. The adsorption capacity approached 24 mg g⁻¹ for the IGX₁₀IL₁₅₀ ionogel, which is comparable to the adsorption of mesoporous styryl-crosslinked vinylimidazolium-based PILs with TFSI anions.^[41] Initially, increasing the IL content slightly increased the adsorption capacity, which can be ascribed to easier gas diffusion in the more swollen ionogels. However, with further increasing of IL content, the adsorption capacity significantly decreased due to a higher mobility of ions at higher degrees of swelling. The evaluation of the effect of crosslinking ratio on CO₂ adsorption of ionogels using QCM-D technique was inconclusive due to the dominant viscous properties of ionogels with low crosslinking ratio.

While QCM-D provides information on CO₂ adsorption of ionogels at the microscale, such information is not always directly relevant to the macroscale CO₂ adsorption of ionogels where gas diffusion becomes an important limiting factor. To investigate the bulk CO₂ adsorption properties of PIL gels, TGA was performed on the ionogels listed in Table 1. The isothermal CO₂ adsorption of ionogels at 50 °C was measured from their mass change when samples were exposed to 100 mL min⁻¹ CO₂ flow. For all ionogels an immediate increase in mass was detected by switching the gas from N₂ to CO₂. This mass increase was reversible when gas was switched back to N₂. Figure 5 shows the CO₂ adsorbed by the ionogels as a function of their IL content (Figure 5a), and crosslinking ratio (Figure 5b). In general, the CO₂ adsorption capacity of the ionogels as a function of IL content obtained by TGA measurements was much lower than that of QCM-D measurements. This effect was due to the significant difference in sample sizes between QCM-D ($\approx 50 \mu\text{g cm}^{-2}$) and TGA ($\approx 600 \text{ mg cm}^{-2}$).

The considerably larger sample size used in TGA measurements significantly reduced the access of CO₂ gas to the bulk of the ionogels. This behavior was also confirmed by comparing the profile of CO₂ adsorption of TGA-tested ionogels as a function of IL content in Figure 5a with those tested with

Figure 4. a) An example of frequency and dissipation change measured by QCM-D over time under CO₂ flow. b) Calculated mass change due to CO₂ adsorption at equilibrium as a function of IL molar ratio. IL and M refer to EMI.TFSI IL and EVI.TFSI monomer, respectively.

Figure 5. Measured mass change due to CO₂ adsorption at equilibrium measured by TGA as a function of a) IL and b) crosslinking molar ratios in ionogels. Arrows indicate the same sample. IL, M, and CL refer to EMI.TFSI IL, EVI.TFSI monomer, and BIS crosslinking agent, respectively. Error bars are smaller than the size of data points.

QCM-D in Figure 4b. In the case of QCM-D, CO₂ adsorption slightly increased by elevating IL content, followed by a continuous decreasing trend. The reduced adsorption of CO₂ at higher levels of IL was attributed to higher ion mobility in the swollen ionogels.^[22] In addition, the heterogeneous structure of the gel network prevents the continuous rearrangement of charged species to accommodate ionic repulsions.^[22] In the TGA measurements, a drop in CO₂ adsorption capacity as a function of IL was observed at slightly higher IL content due to slower diffusion of CO₂ into the dense and less swollen ionogel structure.

The CO₂ adsorption of ionogels as a function of crosslinking ratio followed a similar trend to their conductivity. These measurements were conducted on ionogels with the highest amount of IL content where CO₂ diffusion was less restricted by the network of PIL. Therefore, CO₂ adsorption decreased continuously with increasing ion mobility because of a decreasing crosslinking ratio. The results of QCM-D and TGA studies show that film thickness plays a key role in the gas adsorption. This limiting effect is less critical for swollen ionogels that facilitate the diffusion of CO₂.

Simultaneous CO₂ adsorption and reduction

For CO₂ capture and electrochemical reduction, the gel must combine both large adsorption capacity and high ionic conductivity to function as a solid electrolyte for CO₂ reduction. In addition, the mechanical properties of the ionogel must be optimized to achieve a uniform and stable gel layer covering all electrodes. A prototype device was fabricated from the IGX₁₀IL₂₀₀ ionogel as the adsorbent and electrolyte, with a platinum counter electrode and silver working and reference electrodes (Figure 6a). Silver wire was used as the working

Figure 6. a) Simultaneous CO₂ adsorption and reduction using a solid state ionogel device enclosed in a gas chamber. The photograph of the ionogel device highlights the embedded electrodes (1) as reference: RE, working: WE, and counter: CE, the gasket (2) and the ionogel (3). b) The cyclic voltammetry graph shows current vs. voltage profile of the ionogel under N₂ (broken line) and CO₂ (solid line) blanket. Scale bar is 5 mm.

electrode because this material is known to act as a catalyst for reducing CO₂ to CO at low over potentials with high selectivity and efficiency.^[42] N₂ and CO₂ gases were alternatively passed through the chamber in which the device was placed, and cyclic voltammetry (CV) was performed every 5 min until no further change in the CV profile was observed. The CV profiles of the device after the stabilization of the current under N₂ and CO₂ (Figure 6b) demonstrate that the captured CO₂ was able to diffuse through the ionogel and reached the surface of the electrodes. This is evident from a considerable increase in reduction current ($\approx -1.2 \text{ mA cm}^{-2}$) and a slight decrease in overpotential under CO₂ atmosphere compared with N₂. The CV profile under CO₂ is similar to results obtained previously using silver elec-

trodes in aqueous electrolytes containing an imidazolium IL.^[43]

The reduction current constantly increased during CO₂ purging, reaching its maximum after 20 min of exposure to the gas flow. The observed plateau suggests that the ionogel becomes saturated with CO₂ after about 20 min, reaching a stable condition with maximum CO₂ conversion to CO. The CV profiles were reproducible when the gas line was switched between N₂ and CO₂, suggesting that the device can be continuously regenerated. These results indicate the feasibility of fabricating a solid-state device from suitable ionogels for simultaneous CO₂ adsorption and electrochemical reactions.

Conclusion

An elastic solid-state electrochemical device was designed with dual capacity for the adsorption and electrochemical reduction of CO₂. This device was fabricated from robust poly(ionic liquid) gels swollen with additional ionic liquid to enhance conductivity. The mechanical properties, conductivity, and CO₂ adsorption of ionogels could be controlled by the level of ionic liquid in the ionogels and their crosslinking ratio. High ionic conductivity was achieved by increasing the IL content or reducing the crosslinking ratio. The CO₂ uptake of the ionogels showed a slight increase followed by a gradual decline with increasing IL content. Meanwhile, by increasing the crosslinking ratio, the CO₂ uptake continuously increased. Simultaneous CO₂ adsorption and electrochemical reduction were successfully demonstrated using cyclic voltammetry. This process was reversible and the device was regenerated rapidly after removing CO₂. This study provides a method for the fabrication of solid state devices that combine gas adsorption and electrochemical reactions.

Experimental Section

Materials

For the IL monomer synthesis, 1-vinylimidazole, bromoethane (C₂H₅Br), and lithium trifluoromethanesulfonimide (Li.TFSI), as well as the solvents, methanol (MeOH) and ethyl acetate (EtOAc) were used as received. For polymerization of ionic liquid monomers, *N,N'*-methylenebisacrylamide (BIS, crosslinking agent), α -ketoglutaric acid (UV initiator), *N,N*-dimethylformamide (DMF, solvent), and 1-ethyl-3-methylimidazolium bis(-trifluoromethylsulfonfyl)imide (EMI.TFSI, swelling agent IL) were used. All reagents were purchased from Sigma-Aldrich Australia.

Ionic liquid monomers synthesis

1-Ethyl-3-vinylimidazolium bromide (EVL.Br):^[44] To a solution of 1-vinylimidazole (9.0 mL, 100 mmol) in EtOAc (60 mL) was added bromoethane (14.9 mL, 200 mmol) and the resulting solution was stirred at 50 °C for 24 h. The suspension was allowed to cool to room temperature then the precipitate was collected by filtration. The solids were dissolved in MeOH and the resulting solution was added dropwise to EtOAc (60 mL). The precipitat-

ed product (15.27 g, 75 %) was collected by filtration and used without further purification (**1**, Scheme 1). See Figure S1 in the Supporting Information for NMR spectra.

¹H NMR (400 MHz, D₂O) δ =9.12 (s, 1H); 7.85 (t, *J* 1.8 Hz, 1H); 7.68 (t, *J* 1.8 Hz, 1H); 7.23 (dd, *J* 8.7, 15.6 Hz, 1H); 5.88 (dd, *J* 2.8, 15.6 Hz, 1H); 5.51 (dd, *J* 2.7, 8.7 Hz, 1H); 4.36 (q, *J* 7.4 Hz, 2H); 1.61 ppm (t, *J* 7.4 Hz, 3H).

¹³C NMR (100MHz, D₂O) δ =134.6; 128.9; 123.1; 120.0; 109.9; 45.8; 14.9 ppm.

1-Ethyl-3-vinylimidazolium trifluoromethanesulfonimide (EVI.TFSI):^[45] To a solution of EVI.Br (4.06 g, 20 mmol) in water (10 mL) was added Li.TFSI (7.20 g, 25 mmol). The resulting solution was stirred for 48 h, at room temperature. The lower ionic liquid layer was separated, washed with water, and then dried in vacuo at 50 °C to give the product (7.50 g, 93 %) as a pale yellow oil, which was used without further purification (**2**, Scheme 1). See Figure S2 in the Supporting Information for NMR spectra.

¹H NMR (400MHz, [D₆]DMSO) δ =9.46 (s, 1H); 8.16 (t, *J* 1.8 Hz, 1H); 7.92 (t, *J* 1.7 Hz, 1H); 7.27 (dd, *J* 8.8, 15.6 Hz, 1H); 5.94 (dd, *J* 2.4, 15.6 Hz, 1H); 5.42 (dd, *J* 2.3, 8.7 Hz, 1H); 4.23 (q, *J* 7.3 Hz, 2H); 1.45 ppm (t, *J* 7.3 Hz, 3H).

¹³C NMR (100MHz, [D₆]DMSO) δ =135.0; 128.8; 124.3; 122.9; 121.1; 119.1; 117.9; 114.7; 108.6; 44.6; 14.6 ppm.

Preparation of ionogels

The ionogels were prepared via UV radical polymerization of EVI.TFSI (**2**, Scheme 1) in the presence of BIS crosslinking agent. Briefly, the synthesized EVI.TFSI monomer (450 mg) was added to various amounts of DMF and EMI.TFSI by maintaining the final weight ratio of EVI.TFSI monomer to DMF:EMI.TFSI mixture fixed at 1:1 (i.e. 50 % monomer in solution). To keep the concentration of EVI.TFSI monomer constant throughout the polymerization process and independent of the amount of EMI.TFSI, DMF was used as the diluting solvent and was removed after the polymerization. The BIS crosslinking agent and α -ketoglutaric acid UV initiator were added to the solution and fully dissolved. To evaluate the effect of the degree of crosslinking on the properties of ionogels, the molar ratio of BIS crosslinking agent to EVI.TFSI was varied between 5×10^{-3} and 2.5×10^{-2} (BIS:BIS + EVI.TFSI) at a constant DMF:EMI.TFSI weight ratio of 1:2. The effect of EMI.TFSI as a swelling agent on the ionogels' properties was studied by maintaining the crosslinking ratio at 2.5×10^{-2} and systematically varying the DMF:EMI.TFSI ratio as shown in Table 1. Herein, the crosslinked ionogels swollen in EMI.TFSI are denoted as IGX_{*i*}IL_{*j*}, with *i* and *j* indicating the amount of BIS crosslinking agent and EMI.TFSI, respectively, in the formulation in mg.

The hollow ionogel structure shown in Figure 1b was made as follows: a cotton fabric was wrapped around a glass rod and then soaked in an IL monomer solution. This solution had the same composition as the IGX₂₀IL₂₀₀, except instead of α -ketoglutaric acid UV initiator, ammonium persulfate (Sigma) was used as the thermal initiator. After the cotton reached saturation with the IL monomer solution, polymerization was conducted at 60 °C for 5 h. The middle glass rod was removed after polymerization.

For the mechanical tests and ionic conductivity measurements, respectively, 100 and 50 μ L of each polymerization solution was inserted into sealed transparent plastic tubes with 0.5 cm diameter and UV irradiated for 3 h in a fan-forced UV chamber (Rayonet, UK) equipped with 12 UV bulbs (300 nm). After polymerization, PIL gels were removed from the tubes and placed

over glass slides to remove DMF at 120 °C for 18 h. For CO₂ adsorption studies by QCM-D, 30 µL of polymerization solution was deposited onto gold-coated AT-cut 5 MHz piezoelectric quartz crystals (14 mm diameter) (Qsense, Sweden), and the same curing conditions were used. After drying, the excess ionogel was removed from the surface of the quartz sensors with a spatula and wiped with paper (Kimtech Science). The resulting films were thin and uniform enough for QCM measurements. All the films obtained by this procedure were in the range of 40–50 µg cm⁻² according to frequency change measurements performed before and after their deposition. TGA was performed on PIL gel films with a thickness of approximately 500 µm. For cyclic voltammetry experiments, 90 µL of the IGX₁₀IL₂₀₀ sample was deposited onto a 1.5 × 1.5 cm² glass slide on which silver wires as working and reference electrodes and a platinum wire as the counter-electrode were fixed with a UV-cured acrylate glue. The same acrylate glue was used to construct a 2 mm deep well into which the monomer solution was applied, which was then subjected to the UV irradiation.

Mechanical tests

The mechanical stiffness of PIL ionogels was measured using a Shimadzu EZ-L mechanical tester (Japan) with a 2 N load cell. Indentation tests were performed on 5 mm tall cylindrical PIL ionogels (5 mm in diameter) using a flat stainless steel indenter (990 µm diameter). At the crosshead speed of 0.1 mm min⁻¹, the indenter moved 100 µm from the contact point at the surface of the ionogels. The resulting force versus deformation linear curves were used to calculate the PIL ionogels' Young's modulus (E):^[37]

$$F = (8/3)aEd$$

Here, F and d are force and displacement recorded from the indentation tests and a is the radius of the indenter tip. Measurements were repeated five times.

Ionic conductivity measurements

Ionic conductivity tests were carried out on ≈250 µm thick ionogel samples placed between two 0.07 cm² glassy carbon electrodes. The resistance was measured under an applied 0 V oscillating at 10 kHz and 0.01 V amplitude. The resistance was then converted into ionic conductivity according to:

$$\sigma = L/RA$$

where σ is the ionic conductivity (S cm⁻¹), L is the distance between the two electrodes (cm), R is the measured resistance (Ω), and A is the electrode surface area (cm²). Measurements were repeated three times.

CO₂ adsorption measurements by QCM-D

A Qsense (model E4, Sweden) instrument was used for the measurements of CO₂ adsorption. The quartz sensor containing the deposited ionogel (≈50 µg) was placed in the QCM-D flow cell (QSense, Sweden) and connected to a gas bag (Sigma-Aldrich) containing N₂ or CO₂ at the inlet side and to a peristaltic pump at the outlet side, pulling the gas at 1 mL min⁻¹. Initially, air inside the chamber was removed by closing the inlet and

evacuating the chamber until no change in frequency or dissipation was observed. Then, N₂ or CO₂ was allowed to flow through the chamber. The adsorption capacity of IGX₁₀IL₀ and IGX₁₀IL₁₀₀ was not analyzed with QCM as it was not possible to obtain a uniformly thin film due to the high stiffness of these samples. The experiment was initiated with the valve in the gas bag closed, so any gas in the system was removed, followed by opening the valve to let the N₂ or CO₂ gas flow. The frequency (f) and dissipation (D) changes from the 3rd to 11th harmonics (n) were recorded during the processes.

For the mass of deposited ionogel, the f and D at the different harmonics were measured for the quartz sensors before and after ionogel deposition. As the D values were not significantly different for the different harmonics (less than 5% of f changes), the films were sufficiently thin to be considered piezoelectric rigid and the Sauerbrey equation was used to calculate the mass of the deposited material.^[46]

$$\Delta f_n = -\Delta m/C$$

where C is the mass sensitivity (17.7 ng cm⁻² Hz⁻¹).

The f and D changes due to CO₂ adsorption were fitted using the Kelvin-Voigt model to obtain the mass changes as was previously done for the study of water vapor adsorption by PIL/IL films.^[47]

Thermogravimetric analysis

TGA was performed with a TA Q-5000 instrument connected to N₂ and CO₂ gas lines. Samples were kept under vacuum at 40 °C for 48 h prior to measurement. The temperature was raised from room temperature to 150 °C at a rate of 10 °C min⁻¹ under N₂ flow (40 mL min⁻¹), and was kept at 150 °C for 45 min to ensure all volatile substances were removed. Then, the temperature was decreased to 50 °C (10 °C min⁻¹) and allowed to equilibrate for 30 min, after which gas was switched to CO₂ (100 mL min⁻¹) for one hour. The mass change at this stage was used to calculate physical CO₂ adsorption. Again, the gas was switched back to N₂ while the temperature was held at 50 °C for one hour (physical desorption), then ramped up to 100 °C at the rate of 10 °C min⁻¹. Measurements were repeated three times. The masses of the ionogel samples in the TGA pan were between 4 and 10 mg.

Differential scanning calorimetry

DSC was conducted to measure the glass transition temperature of the ionogels using a TA Instruments DSC, model Q1000. A cyclic heat/cool/heat method was employed under 50 mL min⁻¹ nitrogen flow with heating and cooling rates of 10 °C min⁻¹ from -80 to 200 °C. Samples were dried at 60 °C overnight prior to testing.

Cyclic voltammetry experiments

The solid-state electrochemical cell described above was placed inside a 50 mL plastic chamber that was connected to N₂ and CO₂ gas lines. The gas was allowed to flow for 30 min prior to each cyclic voltammetry experiment. Tests were performed at 50 mV s⁻¹ from -0.2 V to -1.9 V vs. Ag wire using a CH instruments potentiostat model 650D, USA.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] L. C. Tomé, I. M. Marrucho, *Chem. Soc. Rev.* **2016**, *45*, 2785–2824.
- [2] K. Goto, K. Yogo, T. Higashii, *Appl. Energy* **2013**, *111*, 710–720.
- [3] Q. Zhuang, B. Clements, J. Dai, L. Carrigan, *Int. J. Greenhouse Gas Control* **2016**, *52*, 449–460.
- [4] S. Zulfikar, M. I. Sarwar, D. Mecerreyes, *Polym. Chem.* **2015**, *6*, 6435–6451.
- [5] J. M. Huck, L.-C. Lin, A. H. Berger, M. N. Shahrak, R. L. Martin, A. S. Bhowan, M. Haranczyk, K. Reuter, B. Smit, *Energy Environ. Sci.* **2014**, *7*, 4132–4146.
- [6] Y. Zeng, R. Zou, Y. Zhao, *Adv. Mater.* **2016**, *28*, 2855–2873.
- [7] B.-J. Yao, L.-G. Ding, F. Li, J.-T. Li, Q.-J. Fu, Y. Ban, A. Guo, Y.-B. Dong, *ACS Appl. Mater. Interface* **2017**, DOI: <https://doi.org/10.1021/acsami.7b12697>.
- [8] Y. Ban, Z. Li, Y. Li, Y. Peng, H. Jin, W. Jiao, A. Guo, P. Wang, Q. Yang, C. Zhong, W. Yang, *Angew. Chem. Int. Ed.* **2015**, *54*, 15483–15487; *Angew. Chem.* **2015**, *127*, 15703–15707.
- [9] J. Liu, X. Hou, H. B. Park, H. Lin, *Chem. Eur. J.* **2016**, *22*, 15980–15990.
- [10] J. Guzmán, C. Ortega-Guevara, R. G. de León, R. Martínez-Palou, *Chem. Eng. Technol.* **2017**, DOI: <https://doi.org/10.1002/ceat.201600593>.
- [11] Y. Huang, G. Cui, Y. Zhao, H. Wang, Z. Li, S. Dai, J. Wang, *Angew. Chem. Int. Ed.* **2017**, *56*, 13293–13297; *Angew. Chem.* **2017**, *129*, 13478–13482.
- [12] X. Zhu, M. Song, Y. Xu, *ACS Sustainable Chem. Eng.* **2017**, *5*, 8192–8198.
- [13] F. K. Chong, V. Andiappan, D. K. S. Ng, D. C. Y. Foo, F. T. Eljack, M. Atilhan, N. G. Chemsangattuvalappil, *ACS Sustainable Chem. Eng.* **2017**, *5*, 5241–5252.
- [14] X. Luo, Y. Guo, F. Ding, H. Zhao, G. Cui, H. Li, C. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 7053–7057; *Angew. Chem.* **2014**, *126*, 7173–7177.
- [15] G. Cui, J. Wang, S. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 4307–4339.
- [16] M. Gonzalez-Miquel, J. Bedia, C. Abrusci, J. Palomar, F. Rodriguez, *J. Phys. Chem. B* **2013**, *117*, 3398–3406.
- [17] J. F. Brennecke, B. E. Gurkan, *J. Phys. Chem. Lett.* **2010**, *1*, 3459–3464.
- [18] K. M. Gupta, Y. Chen, J. Jiang, *J. Phys. Chem. C* **2013**, *117*, 5792–5799.
- [19] K. N. Ruckart, R. A. O'Brien, S. M. Woodard, K. N. West, T. G. Glover, *J. Phys. Chem. C* **2015**, *119*, 20681–20697.
- [20] Z. Dai, R. D. Noble, D. L. Gin, X. Zhang, L. Deng, *J. Membr. Sci.* **2016**, *497*, 1–20.
- [21] V. Hiremath, A. H. Jadhav, H. Lee, S. Kwon, J. G. Seo, *Chem. Eng. J.* **2016**, *287*, 602–617.
- [22] W. Zhao, G. He, F. Nie, L. Zhang, H. Feng, H. Liu, *J. Membr. Sci.* **2012**, *411–412*, 73–80.
- [23] D. Nikolaeva, I. Azcune, E. Sheridan, M. Sandru, A. Genua, M. Tanczyk, M. Jaschik, K. Warmuzinski, J. C. Jansen, I. F. J. Vankelecom, *J. Mater. Chem. A* **2017**, *5*, 19808–19818.
- [24] T. Wang, K. Ge, Y. Wu, K. Chen, M. Fang, Z. Luo, *Energy Fuels* **2017**, *31*, 11127–11133.
- [25] S. M. Morozova, A. S. Shaplov, E. I. Lozinskaya, D. Mecerreyes, H. Sardon, S. Zulfikar, F. Suárez-García, Y. S. Vygodskii, *Macromolecules* **2017**, *50*, 2814–2824.
- [26] T. Wang, C. Hou, K. Ge, K. S. Lackner, X. Shi, J. Liu, M. Fang, Z. Luo, *J. Phys. Chem. Lett.* **2017**, *8*, 3986–3990.
- [27] M. G. Cowan, D. L. Gin, R. D. Noble, *Acc. Chem. Res.* **2016**, *49*, 724–732.
- [28] S. Soll, Q. Zhao, J. Weber, J. Yuan, *Chem. Mater.* **2013**, *25*, 3003–3010.
- [29] L. C. Tomé, D. Mecerreyes, C. S. R. Freire, L. P. N. Rebelo, I. M. Marrucho, *J. Membr. Sci.* **2013**, *428*, 260–266.
- [30] L. C. Tomé, M. Isik, C. S. R. Freire, D. Mecerreyes, I. M. Marrucho, *J. Membr. Sci.* **2015**, *483*, 155–165.
- [31] M. G. Cowan, M. Masuda, W. M. McDanel, Y. Kohno, D. L. Gin, R. D. Noble, *J. Membr. Sci.* **2016**, *498*, 408–413.
- [32] G. Zhang, G. Wei, Z. Liu, S. R. J. Oliver, H. Fei, *Chem. Mater.* **2016**, *28*, 6276–6281.
- [33] J. Choi, T. M. Benedetti, R. Jalili, A. Walker, G. G. Wallace, D. L. Officer, *Chem. Eur. J. Chem. A* **2016**, *22*, 14158–14161.
- [34] Z. Wang, G. Yang, Z. Zhang, M. Jin, Y. Yin, *ACS Nano* **2016**, *10*, 4559–4564.
- [35] S. Gao, X. Jiao, Z. Sun, W. Zhang, Y. Sun, C. Wang, Q. Hu, X. Zu, F. Yang, S. Yang, L. Liang, J. Wu, Y. Xie, *Angew. Chem. Int. Ed.* **2016**, *55*, 698–702; *Angew. Chem.* **2016**, *128*, 708–712.
- [36] X. Min, M. W. Kanan, *J. Am. Chem. Soc.* **2015**, *137*, 4701–4708.
- [37] S. Naficy, S. Kawakami, S. Sadegholvaad, M. Wakisaka, G. M. Spinks, *J. Appl. Polym. Sci.* **2013**, *130*, 2504–2513.
- [38] L. R. G. Treloar in *The Physics of Rubber Elasticity*, Oxford University Press, Oxford, **1975**.
- [39] M. Delavar, A. A. Ghoreyshi, M. Jahanshahi, S. Khalili, N. Nabian, *RSC Adv.* **2012**, *2*, 4490–4497.
- [40] M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon, J. F. Brennecke, *J. Phys. Chem. B* **2007**, *111*, 9001–9009.
- [41] A. Wilke, J. Yuan, M. Antonietti, J. Weber, *ACS Macro Lett.* **2012**, *1*, 1028–1031.
- [42] T. Hatsukade, K. Kuhl, E. Cave, D. Abram, T. Jaramillo, *Phys. Chem. Chem. Phys.* **2014**, *16*, 13814–13819.
- [43] B. A. Rosen, W. Zhu, G. Kaul, A. Salehi-Khojin, R. I. Masel, *J. Electrochem. Soc.* **2012**, *160*, H138–H141.
- [44] J. Yang, Z. Hua, T. Wang, B. Wu, G. Liu, G. Zhang, *Langmuir* **2015**, *31*, 6078–6084.
- [45] K. Nakamura, T. Saiwaki, K. Fukao, T. Inoue, *Macromolecules* **2011**, *44*, 7719–7726.
- [46] G. Sauerbrey, *Z. Phys.* **1959**, *155*, 206–222.
- [47] T. M. Benedetti, R. M. Torresi, *Langmuir* **2013**, *29*, 15589–15595.

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