Supporting Information

Lewis-acidic water as a new carrier for facilitating CO\(_2\) transport

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Materials and Methods

1. Materials and preparation of liquid and polymer electrolytes

Poly(ethylene oxide) (PEO) (M\(_w\) = 6 x 10\(^5\) Da), carbon-\(^{13}\)C dioxide (99 atom\% \(^{13}\)C, <3 atom\% \(^{18}\)O), lithium trifluoroacetate (CF\(_3\)CO\(_2\)Li, 95%), and deuterium oxide (99.9 atom\% D) containing 0.05 wt.% 3-(trimethylsilyl)propionic-2,2,3,3-d\(_4\) acid sodium salt (deuterated-TSP, d-TSP) were purchased from Sigma-Aldrich. Sodium trifluoroacetate (CF\(_3\)CO\(_2\)Na) was procured from Tokyo Chemical Industry Co., Ltd, while potassium trifluoroacetate (CF\(_3\)CO\(_2\)K, 98%) and hydroxyl terminated poly(dimethyl siloxane) (PDMS) (M\(_w\) = 4200) were purchased from Alfa Aesar.

CF\(_3\)CO\(_2\)-M\(^+\) (M = Li, Na, and K) was added into different solvents to prepare liquid electrolytes. For \(^{13}\)C and \(^{1}H\) NMR, mixtures of H\(_2\)O and d-TSP (4:1, v/v) were used as the solvents, while distilled water was used as the solvent for \(^{39}\)K NMR. Later, carbon dioxide was bubbled for different time intervals depending on the purpose of characterization. In general, 99% pure \(^{12}\)C\(^{16}\)O\(_2\) was used to prepare the samples, except for \(^{13}\)C and \(^{13}\)C DOSY NMR, for which 99% pure \(^{13}\)C\(^{18}\)O\(_2\) was used to clarify the dissolved-CO\(_2\) state.

Polymer electrolyte solutions were prepared as follows. PEO was dissolved in deionized water to form 2 wt.% solutions; in these solutions, CF\(_3\)CO\(_2\)K salt was dissolved as a function of the mole ratio of potassium ion to the number of monomeric units of PEO. The solutions were subsequently vigorously stirred at 353 K for 5 h. The prepared polymer electrolyte solutions were later used to make composite membranes or free-standing films.

2. Material characterization

2.1. Nuclear magnetic resonance (NMR) measurements

2.1.1. \(^{13}\)C NMR and \(^{13}\)C DOSY NMR measurements

Carbon dioxide labeled with \(^{13}\)C was used to sensitively detect the shielding and deshielding of chemical shifts. The general procedure is as follows. \(^{13}\)C\(^{16}\)O\(_2\) (99% carbon dioxide) was bubbled into the prepared liquid electrolytes for 5 s in a valved-NMR tube (purchased from Norell, USA). The prepared gas/liquid mixture was then tightly sealed and in-situ NMR measurements of the formed reversible CO\(_2\) complex were conducted. Deuterated-TSP was used as the internal standard. In the case of \(^{13}\)C DOSY NMR, the diffusion coefficient of
bare CO$_2$ dissolved in neat water was used as the standard value for precise calibration. From the $^{13}$C DOSY NMR results, the apparent sizes of bare and complexed CO$_2$ were estimated using the Stokes-Einstein equation (eqn. (1)), as described in previous studies (1, 2).

$$D = \frac{kT}{6\pi\eta R_s}$$  \hspace{1cm} (1)

where, $\eta$ is the dynamic viscosity of the solvent in which diffusion occurs and $R_s$ is the radius of the diffusing molecular species. $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. $^{13}$C NMR measurements were carried out using a VNMRS 600-MHz instrument (Agilent Technologies, USA). $^{13}$C DOSY NMR measurements were carried out using an Avance III 600MHz NMR instrument equipped with a TCI cryoprobe (Bruker, Germany).

2.1.2. $^{39}$K NMR measurements

Both liquid and gas/liquid mixtures were prepared as described for $^{13}$C NMR. Common $^{12}$CO$_2$ was bubbled through prepared liquid electrolytes for 5 s in capsule-like NMR tubes. Aqueous KCl was used as the reference. The measurements were performed on a Bruker DSX 400 FT NMR instrument (Bruker, USA).

2.1.3. $^1$H NMR measurements

In this case also, both liquid and gas/liquid mixtures were prepared as described for $^{13}$C NMR. $^{12}$CO$_2$ was bubbled through the prepared liquid electrolytes for 5 s, after which $^1$H NMR measurements were conducted on an Avance II 500-MHz Solid NMR instrument (Bruker, Germany).

2.1.4. Reversible complexation of CO$_2$ with hydrated K$^+$ – $^{13}$C NMR spectroscopy

To better understand the reversible complexation of CO$_2$ with hydrated K$^+$ in liquid electrolytes containing CF$_3$CO$_2$K, $^{13}$C NMR analysis of a CO$_2$-complexed solution was conducted as a function of the exposure time to atmosphere. The experimental procedure is as follows. Initially, 5 mL of aqueous CF$_3$CO$_2$K (0.5 M) was poured into a round petri dish (diameter = 5.5 cm and height = 1.5 cm) and $^{13}$C$^{16}$O$_2$ 99% carbon dioxide was bubbled into it for 30 s. After the bubbling was completed, equal amounts of the liquid electrolyte were loaded into four different valved-NMR tubes (purchased from Norell, USA) and $^{13}$C NMR spectra were recorded at different exposure times (10 s, 3 min, 10 min, and 30 min) to the atmosphere (298 K and 40% RH).

2.2. Membrane preparation

2.2.1. Preparation of immobilized liquid membranes (ILMs)

An asymmetric porous cellulose triacetate membrane (HTI Os Mem CTA-ES from Hydration Technology Innovation, USA) was immersed in neat water or 0.5 M CF$_3$CO$_2$K electrolyte for 2 days at 298 K in a temperature controlled-oven. Later, excess solution was wiped off carefully from the membrane surface with a filter paper before installing it in the test cell. The permeation data were obtained over 5 experimental runs and they were found to be highly reproducible, thus verifying that the fabricated membranes were consistent.

2.2.2. Fabrication of thin film composite (TFC) membranes
Thin film composite membranes were prepared as follows. Initially, hydroxyl terminated PDMS was coated onto a naked asymmetrical porous polyacrylonitrile 350 membrane supporter (Nanostone, Germany) to form a highly permeable gutter layer. Later, polymer electrolytes comprising of PEO and CF$_3$CO$_2$K at different mole ratios (1: x, where x ranges from 0 to 1) were coated as selective layers using a coating instrument (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). The effective thickness of the selective layer was confirmed to be ~1.3 μm by scanning electron microscopy (SEM, Fig. S2). Finally, the prepared membrane was dried at 328 K for 1 h.

2.3. Gas permeation and sorption measurements

2.3.1. Gas permeation measurements: constant-pressure, variable-volume method

Gas permeation measurements were conducted in dry and humid conditions at varying feed pressures. The downstream pressure and relative humidity of the humidified gas were fixed at 76.0 cm Hg (atmospheric conditions) and 70%, respectively. The gas flow rates were measured using a bubble flowmeter. The effective surface area of the membrane was 4.906 cm$^2$. A schematic of the experimental set-up for the gas permeation test is shown in scheme S1. The gas permeance ($Q_A$) of component A was determined using the following equation:

$$Q_A = \frac{1}{P_2 - P_1} \frac{273.15}{(273.15 + T)} \frac{P_{atm}}{A} \frac{1}{76} \frac{dV}{dt} \tag{2}$$

where $P_2$ is the upstream pressure, $P_1$ is the downstream pressure (atmosphere condition), $P_{atm}$ is the atmospheric pressure (1 atm), $A$ is the effective area of the membrane, $T$ is the temperature (°C), and $dV/dt$ is the volumetric displacement rate in the bubble flowmeter. The units of gas permeance are GPU, where 1 GPU = 1 x 10$^{-6}$ cm$^3$ (STP)/(cm$^2$ s cmHg).

The ideal separation factor ($\alpha$, permselectivity) of two components is defined as the ratio of their measured gas permeance values.

$$\alpha = \frac{Q_{CO_2}}{Q_{N_2}} \tag{3}$$

$Q_{CO_2}$ and $Q_{N_2}$ represent the permeance values of CO$_2$ and N$_2$, respectively.

2.3.2. Gas sorption measurements

CO₂ gas solubility was measured by a pressure decay method using a dual chamber equipped with a dual transducer sorption apparatus (3, 4) at pressures from 0.5 bar to 2 bar. The sorption measurement apparatus containing two chambers (a sample chamber and a reference chamber) was placed in a temperature-controllable water bath at 298 K. The volumes of the two chambers were carefully calibrated using the Burnett method (3, 5). Pressure changes during sorption measurements were monitored using a pressure transducer (Delta Metrics, Worthington, OH, USA) with a full-scale of 1000 psi and accuracy of 0.05%. A schematic of the design of the sorption apparatus is shown in Scheme S2.

![Scheme S1. Gas permeation measurement apparatus.](image)

Solubility measurements were performed as follows. Pure water (1.0 g) or aqueous CF₃CO₂K electrolyte was placed in the sample chamber and sealed with a VCR gasket. Subsequently, the sample chamber was cooled using liquid nitrogen and degassed for at least 30 min to completely remove any dissolved gas molecules in the liquid samples under vacuum. The sample chamber was then moved to a constant temperature water bath at 298 K. Afterwards, the valve between the sample and reference chamber was closed and the desired amount of gas was charged into the reference chamber. Using the values measured by the pressure transducer attached to the reference chamber along with the known cell volume and temperature, the Soave-Redlich-Kwong (SRK) equation of state was used to estimate the number of moles of gas in the reference chamber; critical parameters from Smith et al. (6) were used for this measurement. The valve was then opened and closed and the released gas was injected into the sample chamber, initiating sorption into the polymer matrix. Pressure decay occurred at a level equal to that of gas sorption. Using the SRK equation of state, a mole balance was established between the initial and equilibrium conditions of the sample chamber so that the number of moles of gas which were sorbed into the samples could be calculated once the chamber pressure was constant (3). Following equilibrium conditions, the reference chamber was pressurized again, gas was injected into the sample chamber, and the sorption measurement was repeated. This process was continued until the pressure was ~2 bar and a sorption isotherm was obtained. From the obtained adsorption quantities, the solubility coefficient was calculated as follows

\[
S(p) = \frac{C}{p}
\]

(4)

where \( S(p) \) is the solubility coefficient, \( C \) is the solubility, and \( p \) is the applied pressure.
2.3.3. Calculation of diffusivity of CO$_2$ through the ILMs

The ratio of the apparent diffusion coefficients of CO$_2$ between the ILMs containing neat water (termed as neat) and CF$_3$CO$_2$K dissolved aqueous electrolyte (0.5 M) (termed as electrolyte) was calculated on the basis of following equation (5)

$$\frac{D_{\text{electrolyte}}}{D_{\text{neat}}} = \frac{P_{\text{electrolyte}} \cdot S_{\text{electrolyte}}}{P_{\text{neat}} \cdot S_{\text{neat}}} = \frac{Q_{\text{electrolyte}} \cdot L_{\text{electrolyte}} \cdot C_{\text{electrolyte}}}{Q_{\text{neat}} \cdot L_{\text{neat}} \cdot C_{\text{neat}}} / \Delta p_{\text{electrolyte}} / \Delta p_{\text{neat}}$$

where $D$, $P$, and $S$ are the apparent diffusion, permeability, and solubility coefficients, respectively, through phase $i$. $Q_i$ is the pressure normalized flux through phase $i$, $L_i$ is the thickness of phase $i$, $C_i$ is the sorbed CO$_2$ concentration in phase $i$, and $\Delta p$ is the CO$_2$ pressure difference applied to the sample. We assumed that the thickness ($L$) and pressure difference ($\Delta p$) across the membrane are identical between neat water and electrolyte-containing ILMs. The pressure difference was actually the same between two samples because we applied the same CO$_2$ pressure during the experiment. The thickness is expected to be similar due to the following two reasons – i) the viscosities of neat water (0.89 cP) and electrolyte (0.90 cP) are similar and ii) the contact angles of neat water and electrolyte solution on a cellulose triacetate membrane are also nearly the same (~70º). Thus, equation S5 can be re-written as follows.

$$\frac{D_{\text{electrolyte}}}{D_{\text{neat}}} \approx \frac{Q_{\text{electrolyte}} \cdot C_{\text{electrolyte}}}{Q_{\text{neat}} \cdot C_{\text{neat}}}$$

3. Scanning electron microscopy (SEM)

Samples from the polymer electrolyte composite membrane were torn off after freezing in liquid nitrogen to obtain SEM images using a Nova nano-SEM 450 instrument (FEI Company, USA).

4. Thermogravimetric analysis (TGA) and Raman spectroscopy

PEO/CF$_3$CO$_2$K polymer solutions were cast onto glass substrates as free-standing films (around 30 µm thick) using a “Doctor blade”. To evaporate the entire water content, the films were dried at ambient conditions for 1 day followed by drying at 60 °C for 3 days in a vacuum oven. TGA experiments were performed on a thermogravimetric analyzer/differential scanning calorimeter (TGA/DSC) instrument (TGA/DSC 1, Mettler Toledo Korea, Republic of Korea) from 50 °C to 500 °C at a heating rate of 10 °C min$^{-1}$ and an inert air gas flow of 50 mL min$^{-1}$. Raman spectroscopy was performed using a Uni-G2D instrument (Uninanotech Co., Ltd., Republic of Korea).
Supplementary data:

Table S1. Effects of CF$_3$CO$_2$K on the state of carbon dioxide in aqueous medium at 298.15 K

<table>
<thead>
<tr>
<th></th>
<th>Initial pH</th>
<th>Final pH</th>
<th>$\Delta$[H$^+$] (mole/L)</th>
<th>[HCO$_3^-$] (mole/L)</th>
<th>Dynamic viscosity (cP) (w/o CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat H$_2$O</td>
<td>6.06</td>
<td>3.889</td>
<td>1.28 x 10$^{-4}$</td>
<td>1.28 x 10$^{-4}$</td>
<td>0.890</td>
</tr>
<tr>
<td>CF$_3$CO$_2$K$^+$/H$_2$O</td>
<td>6.19</td>
<td>4.01</td>
<td>9.71 x 10$^{-5}$</td>
<td>9.71 x 10$^{-5}$</td>
<td>0.901</td>
</tr>
</tbody>
</table>

* CF$_3$CO$_2$K concentration = 0.5 M

$^b$ Final pH was obtained after CO$_2$ bubbling

$^c$ [HCO$_3^-$] = [H$^+$]-[OH$^-$]-2[CO$_3^{2-}$] where the concentration of CO$_3^{2-}$ was negligibly small according to ref. (8).

Figure S1. (A) Pure CO$_2$ permeance and CO$_2$/N$_2$ ideal separation factor of ILMs containing neat water and CF$_3$CO$_2$K electrolyte. (B) Pure CO$_2$ permeance through ILMs containing neat water and aqueous electrolyte (0.5 M CF$_3$CO$_2$M, M = Li, Na, and K) as a function of the applied CO$_2$ pressure.
Figure S2. Deconvoluted $^{13}$C NMR spectra of CO$_2$-bubbled neat water and CF$_3$CO$_2$K electrolyte (0.5 M). (A) Deconvoluted-CO$_2$ peak of neat water. (B) Deconvoluted-carbonate peak of neat water. (C) Deconvoluted-CO$_2$ peak of CF$_3$CO$_2$K electrolyte. (D) Deconvoluted-carbonate peak of CF$_3$CO$_2$K electrolyte.
Figure S3. $^{13}$C DOSY NMR spectrum of 0.5 M aqueous CF$_3$CO$_2$K electrolyte bubbled with CO$_2$ for 5 s. The apparent size was estimated using equation S1.

Figure S4. CO$_2$ solubility in neat water (□) and 0.5 M aqueous CF$_3$CO$_2$K electrolyte (○) as a function of the absolute CO$_2$ pressure.
Figure S5. SEM images of the cross-section of the polymer electrolyte-based TFC membrane comprising of PEO and CF$_3$CO$_2$K.

Figure S6. Concentration of bound-water in CF$_3$CO$_2$K/PEO membranes, as measured by TGA; the water uptake was as high as 64% at a mole ratio of 0.7.
Figure S7. CO$_2$ and N$_2$ permeance of neat PEO exposed to 10% RH and PEO/CF$_3$CO$_2$K (0.7 mole ratio of K$^+$ to the monomeric unit of PEO) at 298 K as functions of the absolute feed pressure at 70% RH.

Figure S8. Correlation between CO$_2$ separation performance and salt concentration at a feed pressure of 1.01 bar (70% RH), 298 K.
Figure S9. $^{13}$C NMR spectra of (A) neat H$_2$O and liquid electrolytes containing (B) CF$_3$CO$_2$Li, (C) CF$_3$CO$_2$Na, and (D) CF$_3$CO$_2$K bubbled with $^{13}$C$^{16}$O$_2$ gas (5 s). The salt concentration of the liquid electrolytes was maintained at 0.5 M. The peaks corresponding to bare and complexed CO$_2$ can be observed at ~124 ppm, while those of the carbonate species can be observed at ~160 ppm.
Figure S9. Raw $^{13}$C DOSY NMR spectra of (A) neat H$_2$O and liquid electrolytes containing CF$_3$CO$_2$K at different concentrations of (B) 0.5 M, (C) 1.5 M, and (D) 3 M. The samples were bubbled with $^{13}$C$^{16}$O$_2$ gas (5 s).

Notes and References