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Dielectric Characterization of H₂O and CO₂ Uptake by Polyethylenimine Films

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ABSTRACT: The absorption of CO_2 by polyethylenimine polymer (PEI) materials is of great interest in connection with proposed carbon capture technologies, and the successful development of this technology requires testing methods quantifying the amount of CO_2 , H_2O , and reaction byproducts under operating conditions. We anticipate that dielectric measurements have the potential for quantifying both the extent of CO_2 and H_2O absorption within the PEI matrix material as well as insights into subsequent reaction byproducts that can be expected to occur in the presence of moisture. The complexity of the chemistry involved in this reactive binding process



clearly points to the need for the use of additional spectroscopic techniques to better resolve the multiple components involved and to validate the model-dependent findings from the dielectric measurements. Here, we employed *noncontact* resonant microwave cavity instrumentation operating at 7.435 GHz that allows for the precise determination of the complex dielectric permittivity of CO_2 films exposed to atmospheres of controlled relative humidity (RH), and N_2 : CO_2 compositions. We find that the addition of CO_2 leads to a considerable increase in dielectric loss of the PEI film relative to loss measured in nitrogen (N_2) atmosphere across the same RH range. We attribute this effect to a reaction between CO_2 and PEI generating a charged dielectrically active species contributing to the dielectric loss in the presence of moisture. Possible reaction mechanisms accounting for these observations are discussed, including the formation of carbamate-ammonium pairs and ammonium cations stabilized by bicarbonate anions that have sufficient local mobility to be dielectrically active in the investigated microwave frequency range. Understanding of these reaction mechanisms and the development of tools to quantify the amount of reactive byproducts are expected to be critical for the design and optimization of carbon capture materials.

INTRODUCTION

The mitigation of greenhouse gas emissions, particularly carbon dioxide, is a global imperative to combat climate change and transition toward a sustainable future.^{1,2} Carbon capture and storage technologies have emerged as promising approaches to reduce CO₂ emissions from various industrial processes and power generation.³⁻⁵ Among these technologies, the use of polymeric amine-containing materials, such as branched polyethylenimine (PEI), for CO_2 sorption has attracted considerable attention as a versatile and practical carbon material due to its considerable CO₂ capture capacity, reasonable cost, and relative ease of regeneration.⁶⁻⁹ Understanding the PEI sorption mechanisms and the nature of the binding interactions with CO₂ under the variable humidity conditions encountered in practice is critical for designing efficient CO₂ capture systems.¹⁰ However, probing these interactions at the molecular level can be challenging and is particularly complicated by reactive phenomena arising from the presence of water vapor and the presence of an added structural silica support. $^{11-15}$

There is a long history of using noncontact radar and dielectric spectroscopic methods to estimate moisture content in complex systems as the water content of soils,¹⁶⁻¹⁸ and building materials such as concrete, masonry, composites, wood, and the asphalt material of roads,¹⁹⁻²² and in a wide

range of agricultural applications.¹ In our previous work, we employed a high-resolution noncontact dielectric microwave cavity to quantify and control confinement of absorbed water in cellulose nanocrystal materials,²³ hydration number of water-sensitive fluorogenic dyes,²⁴ and to characterize dielectric properties of epitaxial 2D graphene.^{25,26} Inspired by these prior studies, the present paper explores the potential of a noncontact resonant microwave cavity-testing method to precisely monitor the complex dielectric permittivity (ε^*) of PEI samples exposed to a mixture of N₂ and CO₂ gas under different controlled levels of relative humidity (RH). It is our belief that dielectric characterization might serve as a versatile platform for monitoring and studying the sorption of CO₂ on various classes of amine absorbers.

The Results and Discussion section presents the real and imaginary parts of the dielectric permittivity relative to air ($\varepsilon_{r'}$ and $\varepsilon_{r''}$) of PEI samples measured under different conditions,

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including exposure to CO_2 under varying RH levels. The dielectric measurements reveal that the absorption of CO_2 in the presence of humidity involves the formation of a charged complex involving CO_2 , PEI, and water that is dielectrically active over a large range of RH.

The existence of this reactive species is clearly relevant to any methodology aimed at quantifying the molecular binding of sorbate molecules to these materials. The present work emphasizes evidence of the presence of this reactive species and its molecular origin. This information should be useful, in conjunction with other spectroscopic information, in creating a suite of noninvasive measurements that can serve as an effective metrology for fully characterizing the molecular species in PEI materials utilized in applications as a practical carbon capture material. In particular, we are currently exploring the use of infrared spectroscopy and gravimetric measurements to independently estimate the water and CO_2 concentration in the PEI films and some preliminary results are mentioned with regard to interpreting our dielectric cavity measurements.

EXPERIMENTS

Sample Preparation. Branched PEI, having linear form H- $(\text{NHCH}_2\text{CH}_2)_n\text{NH}_2$, average $M_w \sim 25,000 \text{ g/mol}$ by low angle light scattering (LALLS), and average molecular weight, $M_n \sim 10,000$, by gel permeation chromatography (GPC), was obtained from Sigma-Aldrich.[‡] For the dielectric measurements, samples were dissolved in ethanol to prepare a 75 mg/mL solution. The solution was cast onto silica substrates (20.0 mm × 8.0 mm × 207 μ m) to obtain a 500 nm thick coating on each side. After film casting, the samples were dried at room temperature for about 3 h under N₂ and the thickness was measured by ellipsometry. Before the dielectric measurements, the samples were further conditioned overnight under dry nitrogen inside of the environmental enclosure (Figure 1) and at a temperature of 24 °C until a dry plateau in the dielectric constant (ε_r ') was achieved.

Dielectric Characterization. Measurements of complex dielectric permittivity ($\varepsilon^* = \varepsilon_r' - j\varepsilon_r''$) were carried out on PEI films at room temperature at 24 °C under N₂ and under a mixture 95% N₂:5% CO₂ (by mol %) as a function of RH using a noncontact resonant microwave cavity. This method is nondestructive and experimentally simple, and it does not require any electrical contacts that would



Figure 1. Microwave cavity test fixture. (1) WR90 waveguide resonator, (2) cross-polarized waveguide-to-coaxial couplers with coaxial connections to a vector network analyzer, (3) specimen, (4) specimen holder with sealing gasket, and (5) environmental enclosure.

otherwise obscure the water/CO2 sorption and its effect on the PEI dielectric properties. Our cavity-testing fixture is made of 127 mm long, rectangular waveguide (WR) with an internal width of 2.3 cm (0.90 in.) and an internal vertical height of 10 mm; this geometry is referred to as WR90 standard. The waveguide is impedance terminated with near cross-polarized coaxial-to-WR90 couplers on both sides, creating a standing wave, i.e., resonance due to the superposition of transmitted and reflected waves. The testing fixture is connected to a vector network analyzer (Agilent N5225A[‡]), which measures the transmission scattering parameter, S₂₁, of the resonant peak, the resonant frequency, f_{xy} and the half-power bandwidth, Δf_{x} . The cavity operates at microwave frequencies ($f_0 = 7.435$ GHz) in the transverse electric field mode $(TE_{1,0,3})$, where the electric field attains a maximum value at the cavity center. The experimental apparatus operating inside an environmental enclosure is shown in Figure 1.

In our earlier work, 25,27 we showed that the classical perturbation model for a small specimen inside a rectangular cavity operating in the TE_{1,0,n} resonant mode can be simplified to linear expressions:

$$y' = (e_r^r - 1)2x - b'$$
 (1a)

$$y'' = \varepsilon_{\mathbf{r}}^{''} 4x - 2b'' \tag{1b}$$

The real permittivity, ε_r' , and the dielectric loss, ε_r'' , can then be determined from the consequent slopes of eq 1a, where intercepts b' and b'' are constant. The parameters x, y', and y'' in eq 1b are defined through the following relations:

$$x = V_x/V_0, y' = (f_0 - f_x)/f_0, \text{ and } y'' = 1/Q_x - 1/Q_0$$
 (2)

where f_0 and Q_0 are the resonant frequency and quality factor of the empty cavity having the volume V_0 . Correspondingly, the value of f_x and Q_x , then represent the resonant frequency and quality factor in the cavity with the specimen volume, V_x . The quality factor ($Q = f_r/\Delta f$) is a dimensionless parameter describing the ratio of energy stored in the resonant circuit to time-averaged power loss of the cavity, or equivalently, a resonator's half-power bandwidth, (Δf) relative to the resonant frequency (f_r).

The cavity-testing fixture is mounted inside an environmental enclosure, enabling measurements under a controlled RH, N₂, and CO₂ atmosphere. During measurements, the specimen is inserted into the cavity through a small slot machine in the center of the cavity. The specimen dimensions (width (w), thickness (t), and height (h)) should be uniform. Insertion of a specimen in volume steps $(V_{x-} = w t$ h_x causes the resonant peak to shift to lower frequencies f_x in proportion to ε_r' , while the corresponding quality factor, $Q_x = f_x / \Delta f_x$, decreases in proportion to ε_r'' , Δf_x is the resonator's half-power bandwidth, relative to the resonant frequency f_x . Typically, 40 pairs of data points, f_x and Q_x , are collected, while h_x increases in steps from 0 to $h_{\text{max}} = 10$ mm, where h_{max} is the inner vertical dimension of the WR90 waveguide. This approach makes each step (i) equivalent to the measurement of separate specimens of different volumes $V_x(i)$ exposed to the same RH/CO₂ atmosphere. The (f_x) and (Q_x) data points are then fitted to the linear portion of eqs 1a, where slope eq 1a corresponds to $\varepsilon_{\rm r}{}'$ and the slope of eq 1b corresponds to $\varepsilon_{\rm r}{}''$ measured with typical uncertainty in ε_r' and ε_r'' of $\pm 10^{-4}$ (for uncertainty evaluation see Supporting Information, pages 1-4).

The total active volume of the 500 nm thick PEI coated on both sides of the 8.0 mm wide SiO₂ substrate (Dielectric Characterization section) that is being measured inside the microwave cavity is $\approx 8 \times 10^{-5}$ cm³.

During measurements, the specimen is exposed to N_2 and N_2 :CO₂ mixture while the humidity is adjusted from RH near 0.5–50% at an average rate of 0.1% per min with 4 min equilibration time, where uncertainty in RH value measured by the sensor located at the specimen is $\pm 1\%$.

RESULTS AND DISCUSSION

Figure 2 shows the real part of the dielectric permittivity, ε_r' , measured as a function of RH for bare silica substrates and for



Figure 2. Real part of the dielectric permittivity (ε_r') as a function of RH for bare silica substrate under nitrogen gas (triangles, SiO₂), PEI specimens under nitrogen gas (N₂) (squares) and under gas mixture 95% N₂:5% CO₂ (circles). The straight lines represent linear fits over the data points. The relative uncertainty of individual data in ε_r' is $\pm 1.3 \times 10^{-4}$. The apparent scattering of data points results from uncertainty in RH measurements, which is mitigated by the linear fits.

PEI samples under nitrogen and under a nitrogen–carbon dioxide mixture. For clarity of discussion that follows, we simply assume a linear dependence of e_r' vs RH.

It is evident that the absorption of water ($\varepsilon_{r'H2O} \approx 78$) by a low dielectric constant specimen leads to an increase in $\varepsilon_{r'}$. In the case of SiO₂ substrates ($\varepsilon_{r'} \approx 3.53$), the effect of increasing RH on $\varepsilon_{r'}$ is small. When RH increases from 0 to 50%, $\varepsilon_{r'}$ of SiO₂ increases by about 0.001, indicating that the moisture absorption of SiO₂ is negligible. In comparison, the effect of moisture on the $\varepsilon_{r'}$ of PEI samples is considerably larger. Under a N₂ atmosphere at RH of 50%, $\Delta \varepsilon_{r'} \approx 0.014$, and therefore can be used to determine the amount of water adsorbed by the PEI specimens. It is seen in Figure 2 that the addition of CO₂ causes $\Delta \varepsilon_{r'}$ to increase slightly with increasing RH beyond that of N₂, suggesting that either more water is sorbed or that moisture activates dielectric polarization interactions between CO₂ and PEI.

The volume fraction of water f_c absorbed by PEI films is determined from the ε_r' data measured under N₂ (Figure 2), using Maxwell-Garnett dielectric mixing rule²⁸ (see Supporting Information for details). In solving the mixing rule for f_{c} , we consider that absorbed water is bound to the PEI matrix that decreases $\varepsilon_{\rm r\,\,H2O}^{\,\prime}$ from its free value of 78 to about 60, which is consistent with numerous other dielectric measurements of polar substrates exposed to moisture.²³ The results are then normalized for f_c that accounts only for water absorbed within the volume of the PEI film. This eliminates the dielectric volume effect of the SiO₂ substrate. Molar concentration of water in PEI samples is calculated as a product of f_c and the volume of PEI, which then is normalized to molecular mass of water (\cong 18 g/mol). The result of simple linear fitting of the dielectric response of Figure 2 can be transformed to estimate the adsorbed water volume fraction shown in Figure 3, which agrees with results measured via a quartz-crystal microbalance (QCM) up to RH of about 35% (see Supporting Information for details).

The water volume fraction increases with an increase in RH in proportion to the measured value of ε_r' . At RH of 35% the volume fraction of water is about 0.18. Since the specific mass density of PEI is 1.03 g/cm³, the water mass uptake is 0.18 g-H₂O/g-PEI. The corresponding molar amount of water (n_{-H2O}) in PEI samples is 0.01 mol-H₂O/g-PEI.



Figure 3. Volume fraction of water in PEI as a function of the relative humidity (RH). The error bars represent combined relative uncertainty values. The line is to guide the eyes over the data points and reflects the assumed linear dependence of $\varepsilon_{r'}$ vs RH shown in Figure 2.

Figure 4 shows the imaginary part of the dielectric permittivity, ε_r'' , (dielectric loss) measured for PEI specimens



Figure 4. Imaginary part of the dielectric permittivity (ε_r'') measured as a function of RH for PEI specimens under mixture of 95% N₂:5% CO₂ (circles) and under nitrogen gas (N₂, squares). The corresponding solid lines with symbols represent fittings to arbitrary functions through the data points. The solid line, $\Delta \varepsilon_r''$, represents ionic concentration upon introduction of CO₂, which approaches a saturation level at RH of about 35%.

as a function of RH, under nitrogen gas (N_2) and while exposing to carbon dioxide in a mixture of 95% N_2 :5% CO₂.

It is seen in Figure 4 that the measured dielectric loss of PEI under the CO_2-N_2 mix is larger than that under N_2 within the RH range between 1 and 50%. The difference between the dielectric loss of PEI exposed to the CO_2-N_2 mix versus N_2 with respect to RH,

 $\Delta \varepsilon_r'' = \varepsilon_r''_{CO2} - \varepsilon_r''_{N2}$ quantifies the sorption effect of CO₂. We interpret this change to arise from the generation of ionic species that affects the response of water in the PEI specimens with the introduction of CO₂. Charged moieties are detectable in our dielectric measurement at RH above 0.5% (Figure 4 plot CO₂-N₂), suggesting that the increase in $\varepsilon_r''_{CO2}$ over that of $\varepsilon_r''_{N2}$ can be attributed to a hydrated ionic complex. With increasing RH, the dielectric loss data plotted in Figure 4 show a considerable increase in ε_r'' in the presence of CO₂, up to a saturation level at RH of about 35%, indicating that the molecular mechanism involves the formation of an ionic complex between CO₂ and PEI that is mediated by water.

Application of noncontact microwave dielectric testing allows us to determine complex permittivity ($\varepsilon^* = \varepsilon_r'$ – $i\varepsilon_r''$) of PEI with increasing moisture and CO₂ uptake for a mixture of 95% N2:5% CO2. The two independent dielectric permittivity parameters ε_{r}' and ε_{r}'' reflect different dielectric processes at the molecular level. The real part of complex permittivity, $\varepsilon_{\rm r}'$, is primarily due to the density of electrical dipoles involved in rotational dynamics synchronized (in phase) with the applied microwave field. The imaginary part of complex permittivity, ε_{r} ", is the measure of the dielectric loss due to charged molecules that lag in phase behind the applied microwave electric field.^{29,30} Water molecules, having relatively large dipole moments and relaxation frequencies extending up to 20 GHz, actively contribute to the measured ε_r '. From the $\varepsilon_{\rm r}'$ data (Figure 2), we can quantitatively determine the volume fraction and concentration of water in PEI under a N2 atmosphere as shown in Figure 3. At a RH = 35%, the water mass uptake by PEI is about 0.18 g-H₂O/g-PEI. In contrast, CO2 does not have an active dipole moment itself, rendering its contribution to $\varepsilon_{\rm r}'$ within the detectability limit of dielectric testing. However, the dielectric loss data (ε_r) shown in Figure 4 demonstrate convincing sensitivity to CO₂ uptake in PEI above RH 0.5% when water is present. The reaction between CO₂ and PEI in the presence of moisture leads to a reaction product that increases ε_{r} " values beyond that attributed to water absorption alone. We interpret this change to arise from the generation of ionic species that affects the response of water in the PEI specimens with the introduction of CO₂.

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Previous work shows that branched polyethylenimines, such as PEI, can form ionic complexes with CO_2 in the presence of water $^{11,12,32-34}$ and the occurrence of this type of complex in our PEI film naturally leads to the change in the dielectric loss (Figure 4). We can make an order of magnitude estimate of water content in the complexed state by taking into account the existence of this complex formation and its expected dielectric consequences in our modeling of the dielectric response. Assuming that the charge transfer complex formed through the reaction between CO₂ and PEI is solvated by a small, but constant number n_s of hydrating water molecules (we would guess about 2 or 3 water molecules, but the exact number remains to be established by simulation and or direct measurements), then we would expect the formation of a $1:n_s$, CO₂:H₂O complex. This assumption seems plausible for a rough estimate of the amount of complexed water with CO₂ in the PEI film that is responsible for the observed changes in ε_r'' . Based on this simple tentative model, we may then estimate the concentration of complexed CO₂ in the PEI material as a function of RH. Accordingly, we find at RH of 35% the $\Delta \varepsilon_{\rm r}{''} \approx$ 7.85×10^{-4} and the corresponding value under a N₂ atmosphere, $\varepsilon_{\rm r}''_{\rm H2O} \approx 1.4 \times 10^{-3}$. This would indicate a complexation concentration ratio of $[CO_2]:[H_2O] \approx \Delta \varepsilon_r''/$ $\varepsilon_{\rm r''H2O} \approx$ 0.6, which seems plausible. At a RH of 35%, the molar concentration of water in PEI samples is 0.01 mol-H₂O/ g-PEI, thus the concentration of captured CO_2 , n- $_{CO2}$ = $0.6n_{\rm H2O} \approx 6 \times 10^{-3}$ mol-CO₂/g-PEI or capture capacity of 6 mmol CO₂/g-PEI (0.26 g-CO₂/g-PEI). With increasing RH above 35%, the adsorption capacity decreases approaching zero at RH \approx 50%. The concomitant increase in the dielectric response in PEI films with the increase of RH may be used as a means of characterizing the water uptake in an unreactive environment and provide insight into CO₂ uptake through the evidence of ionic species at 35% RH, which then neutralizes at higher RH conditions. Under humid conditions, and whether

water becomes a competitive nucleophile attacking the electrophilic CO_2 , amines can react with CO_2 and H_2O to form ammonium ions and bicarbonate, enhancing considerably adsorption capacity compared to the dry conditions.³³ Thus, in the presence of moisture PEI can react with CO_2 gas creating bicarbonate anions complexed with primary, secondary, and tertiary ammonium cations, which then neutralize with increasing water uptake,^{8,12,33} as illustrated in Figure 5.



Figure 5. Examples of reaction schemes of CO_2 adsorption by PEI films, $[(R)NH_2]$, on a SiO₂ substrate under humid conditions.

These reaction schemes are typical examples of the potential reaction paths that can explain our experimental results. The actual reaction mechanism at varying moisture levels and dry conditions may involve intermediate complexes, such as ammonium carbamates, ^{11,12,34,35} and can be more convoluted than the schemes shown in Figure 5 (see Supporting Information, page 8). Further measurements are required to confirm our preliminary finding and to determine if a correlative relationship can be obtained between dielectric and independent measurements as well as improved modeling studies to validate reaction mechanisms considering these data.

We note that there has been extensive study of hydration in epoxy materials, whose chemistry is somewhat similar to PEI.^{36–38} Measurement and simulation studies point to reactive hydrolysis,³⁸ oxidative mechanisms,³⁹ and it seems likely that this phenomenon might also arise in PEI materials being developed for CO₂ capture. The utilization of dielectric measurement to monitor these reactive by-products might be useful in developing successful strategies for monitoring the integrity of these materials for use in field conditions.

CONCLUSIONS

In this work, we investigate the complex dielectric permittivity of PEI films supported on silica substrates exposed to a nitrogen-carbon dioxide gas mixture of 95% N₂:5% CO₂. The dielectric measurements were carried out over RH values 0% to up to 50% at a constant temperature of 24 °C using a noncontact resonant microwave cavity operating at 7.435 GHz. This novel instrumentation allows for direct characterization of CO₂-PEI complexation by measuring the permittivity of PEI films under a controlled humidity-nitrogen atmosphere with and without CO_2 present. We find that the addition of CO_2 leads to a considerable increase in the dielectric loss $(\Delta \varepsilon_r'')$ of the PEI films, relative to loss measured under nitrogen (N_2) atmosphere across the same RH range. With increasing humidity, $\Delta \varepsilon_{\rm r}''$ increases showing a maximum at RH of about 35%, which corresponds to a capture capacity of 6 mmol CO₂/g-PEI (0.26 g-CO2/g-PEI). Furthermore, our results indicate that the molecular mechanism involves the formation of an ionic complex between CO₂ and PEI that is mediated by water. We attribute this effect to a reaction between CO_{21} H₂O, and PEI generating ammonium cations complexed with

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bicarbonate anions,^{8,32–34} which have sufficient local mobility to be dielectrically active in the microwave frequency range of 7 GHz. With increasing RH beyond 35%, $\Delta \varepsilon_r''$ decreases indicating that after saturation, the concentration of the dielectrically active complex becomes effectively neutralized as RH advances toward 50%. Further measurements are required to confirm this preliminary finding and to determine if a correlative relationship can be obtained between dielectric and independent measurements, as well as improved modeling studies to validate reaction mechanisms considering these data. It is anticipated that understanding the reaction mechanism of CO_2 with the PEI matrix in the presence of water could lead to significant advances in the development and utilization of CO_2 sorption materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.4c00247.

Uncertainty of dielectric measurements; dielectric mixing rule; comparison of water uptake measurement by the dielectric and quartz-crystal microbalance methods; and reaction scheme: single and double amine mechanisms (PDF)

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Notes

The authors declare no competing financial interest.

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