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Cellulose based poly(ionic liquids): Tuning cation-anion interaction to improve carbon dioxide sorption



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ABSTRACT

Mitigation of climate change is an urgent agenda. Development of materials from agroindustrial residue to be used as sorbents for CO₂ capture is a significant goal to be achieved both for environmental protection and resource utilization. In this work, cationic cellulosic poly(ionic liquids) PILs using cellulose extracted from rice husk were synthesized. Imidazolium and ammonium were evaluated as cations combined with different counter-anions (chloride [Cl]⁻, tetrafluoroborate [BF₄]⁻, hexafluorophosphate [PF₆]⁻ or bis(trifluoromethanesulfonyl) imide [TF₂N]⁻). Synthesized PILs were characterized by nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), universal attenuated total reflectance sensor (UATR-FTIR), thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM). Reusability and CO₂ sorption capacity were performed by pressure decay-technique. Competitive atom-atom coordination was investigated by semi-empirical molecular dynamics simulations, PM7-MD simulations. PILs showed a high CO₂ sorption capacity directly influenced by anion. At 3 MPa of CO₂ pressure the sorption capacity increases in the following order for both cations [Cl]⁻ < [BF₄]⁻ < [TF₂N]⁻ < [PF₆]⁻. Computational modeling suggests that TF₂N blocks important CO₂ binding sites. The best sorption value was found for PIL [CelEt₃N][PF₆] of 38 mg/g at 0.1 MPa and 168 mg/g at 3 MPa at 25 °C. The recycling experiments of CO₂ sorption demonstrated a good reusability of synthesized PILs for CO₂ sorption.

1. Introduction

Carbon capture technologies emerge as one of the main strategies to reduce CO₂ emissions and mitigate the climate change effect [1–11]. Development of versatile materials for CO₂ separation from exhausted gases has become one of the main research niches in this area [6,8,12,13].

Amines aqueous solutions stand out as the benchmark solvent for CO₂ separation from exhaust gases [14–19] and natural gas [14,15,17,20]. However the use of these solvents presents operational drawbacks such as high energy consumption in regeneration stage, corrosive products formation as well as additional operational costs due to solvents substitution as a consequence of degradation [14,16,18,19,21].

Poly (ionic liquids) or polymeric ionic liquids (PILs) have shown potential for CO₂ capture [11,20–26]. These functional polymers

present an ionic liquid (IL) moiety on each repeated unit [8,12,22]. ILs polymerization resulted in increased CO₂ capture efficiency. PILs present higher CO₂ sorption capacity, faster sorption/desorption kinetics once compared to ILs [27]. PILs synthesis is carried out following these main routes: IL monomers direct radical polymerization, polycondensation and/or polymers modification [8,28,29]. Among these routes the latter is extremely attractive allowing the use of commercially available polymers.

Different PILs obtained via polycondensation and/or polymers modification have been reported as well as their use in CO₂ capture. Literature describe PILs based on polybenzimidazoles [29–31], polyimides [28], poly(ether ketone)s [32] and polyurethane [33–35].

Cellulose is a versatile low cost natural polymer [36,37]. The possibility of its structural chemical modification by reaction with available hydroxyl groups allows its application in several areas [36–38]. World rice crop is estimated at 500 million tons per year. The rice husk

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is the main agroindustrial residue generated in this cereal processing [39,40]. The use of this residue as raw material source to obtain cellulose based PILs may reduce waste generation and produce low cost sorbents [41].

We have recently reported the synthesis of cellulose based anionic PILs and their ability to capture CO₂ [41]. PILs were obtained by chemical modification of cellulose fibers extracted from rice husk. Four different ionic liquids (IL) counter-cations were introduced (imidazolium, phosphonium, ammonium and pyrrolidinium) [41]. Cellulose based PILs were presented as a promising approach for CO₂ capture. Yet, counter-cation introduction into cellulose structure promoted increased CO₂ solubility and a completely reversible CO₂ sorption/desorption process. The best sorption result was obtained with ammonium as counter-cation (CL-TBA) [41].

A different approach was used to obtain cellulosic PILs in this work. Unlike our first work cationic cellulosic PILs were synthesized. PILs were obtained with imidazolium or ammonium cation, using different counter-anions ([Cl][−], [BF₄][−], [PF₆][−] or [TF₂N][−]). In addition, PM7-MD simulations were used to understand the competitive atom-atom coordination.

2. Experimental section

2.1. Materials

Rice husk was donated by Cooperativa Arrozeira Extremo Sul Ltda. Sodium hydroxide (NaOH, 97% Vetec), hydrogen peroxide (H₂O₂, 35%, Neon), sulfuric acid (H₂SO₄, F.Maia, P.A), Thionyl chloride (SOCl₂, 99%, Aldrich), ammonium hydroxide solution (30–32%, Vetec) 1-Methylimidazole (Aldrich, 99.0%), Triethylamine (99%, Vetec), Lithium(I) bis(trifluoromethanesulfonyl)imide (LiTF₂N, 99%, Aldrich), Sodium tetrafluoroborate (NaBF₄, 98%, Aldrich), Sodium hexafluorophosphate (NaPF₆, 98%, Aldrich) and *N,N*-dimethylformamide (DMF, 99.5%, Merck) were used as received.

2.2. Cellulose extraction and modification

Cellulose fibers extraction procedure from rice husk was adapted from literature [42,43]. Fibers were obtained by submitting rice husk to alkali (NaOH) and acid (H₂SO₄) treatments followed by bleaching (H₂O₂/NaOH). Cellulose extraction details are well reported elsewhere [41].

Cellulosic based Poly (ionic liquid)s (PILs) syntheses were performed in a three steps process as shown in Fig. 1. The experimental procedure was based on literature [44–47].

Initially, cellulose was chemically modified with SOCl₂ to obtain chlorinated cellulose (6-chloro-6-deoxycellulose, CDC) (Fig. 1a). A sample of 10 g of cellulose fiber was suspended in DMF (200 mL) followed by the slow addition of 35 mL of thionyl chloride (SOCl₂) at 80 °C under mechanical stirring. After the addition was complete, the reaction was kept for 2.5 h at 90 °C. The viscous solution was cooled to room temperature and poured into iced water (500 mL) under stirring. The precipitated (CDC) was treated with several aliquots of ammonium hydroxide solution and washed with water to bring the pH to neutral. The CDC was then separated by filtration and dried under vacuum at 60 °C. In the next step, a sample of CDC (4 g) was reacted with 40 mL of 1-Methylimidazole (at 100 °C) or Triethylamine (at 80 °C) and kept under stirring for 24 h. The cellulose based PILs ([Celmim][Cl] or [CelEt₃N][Cl]) obtained from this reaction were precipitated using methanol and then dried under vacuum at 60 °C. Finally, to exchange chloride from ([Celmim][Cl] or [CelEt₃N][Cl]) by another anion, lithium or sodium salt of the corresponding anion was used. The ion exchange step was performed at room temperature with stirring for 24 h using saturated solution of LiTF₂N, NaBF₄ or NaPF₆ (Fig. 1b).

2.3. Characterization

The synthesized materials were characterized by Universal Attenuated Total Reflectance sensor (UATR-FTIR) using Perkin-Elmer Spectrum 100 FTIR Spectrometer, 4000–650 cm^{−1} wavenumber range. The solid-state ¹³C NMR spectra were obtained with a Bruker Avance DRX-400 spectrometer at 400 MHz. Field emission scanning electron microscopy (FESEM) analyses were performed using a FEI Inspect F50 equipment in secondary electrons (SE) mode. Thermogravimetric Analysis (TGA) was performed using TA Instruments SDT-Q600 between 25 and 500 °C with a heating rate of 10 °C/min in a nitrogen atmosphere. Powder X-ray diffraction (XRD) pattern was recorded by Bruker-AXS D8 ADVANCE diffractometer operated at 40 kV voltage and 20 mA current using Cu Kα radiation (λ = 1.5406 Å), 3–40° range with 0.02 step and 1.0 min scanning time. To evaluate the surface composition of the cellulosic poly (ionic liquids), experiments by X-ray photoelectron spectroscopy (XPS) were carried out with a XPS/ISS/UPS-ACenteno surface characterization platform built by SPECS (Germany). The platform is equipped with PHOIBOS 150 2D-DLD energy analyzer. A monochromatic Al Kα X-ray source (FOCUS 500) operated at 200 W was used for measurements. The pass-through energy of the hemispherical analyzer was set at 100 eV for the general spectra and 60 eV for high resolution spectra. The surface charge compensation was monitored with a Flood Gun device (FG 15/40-PS FG500) operated at 58 μA and 2 eV. High-resolution spectra of the elements found were recorded for quantification, CasaXPS software was used for spectral analysis and curve fitting using C-C signal position at 285 eV as Ref. [47–49].

2.4. Sorption measurements

CO₂ sorption capacity was assessed by pressure-decay technique at 25 °C and 0.1–3 MPa using a dual-chamber gas sorption cell [50]. The experiments were carried out in triplicate. The sorption apparatus equipped with a vacuum Pump (Edwards RV5) and housed in a thermostatic oil bath (Julabo – ED/0.01 °C), consists of a gas chamber and a sorption chamber where the samples are placed. The schematic sorption apparatus is shown in Fig. 2. Operation of such device was reported elsewhere [51,52]. Samples were weighted (1.0–1.5 g), moved to sorption chamber and subjected to 10^{−3} mbar vacuum at 25 °C during 1 h. CO₂ (air liquid/99.998%) was admitted into the reservoir at desired pressure and allowed to enter the sorption chamber.

Gas sorption at equilibrium was determined from the difference between the initial and final number of moles of gas using Eqs. (1) and (2), respectively. The gas mass adsorbed in the sample is denoted as WCO₂/g

$$n_{CO_2} = \frac{p_i V_{gc}}{Z_{(p_i, T_i)} R T_i} - \frac{p_{eq} (V_t - V_p)}{Z_{(p_{eq}, T_{eq})} R T_{eq}} \quad (1)$$

$$w_{CO_2/g} = \frac{n_{CO_2} M}{W_s}, \quad (2)$$

where V_{gc} is volume of the gas chamber, p_i and T_i are pressure and temperature in the gas chamber, p_{eq} and T_{eq} are pressure and temperature at equilibrium. V_p is volume of the sample, V_t is total volume of the sorption cell, Z is compressibility factor for the pure gas calculated by the Span-Wagner equations-of-state for CO₂ (Equation: converging the fluid region at the triple-point temperature up to 26.85 °C at pressures up to 800 MPa) [53].

2.5. Computer simulations

Semi-empirical molecular dynamics simulations, PM7-MD [54–62] were performed to investigate atom-atom coordination. The wave function convergence criterion was set to 10^{−7} Hartree with the Slater basis set. The equations-of-motion were propagated with a time-step of

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