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Electrode-Modified Block CoPoly-Ionic Liquid Boosting the CO₂ Reduction toward CO in Water-based Media

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Coupling polymer and ionic liquids with electrodes for catalysis is a promising tool for optimization of electrocatalytic CO₂ reduction reaction (CO₂RR). Here, block copolymer ionic liquids BCPIILs were synthesized *via* controlled radical polymerization and nucleophilic post-substitution to introduce imidazole moieties. We show that, thanks to these PIL functionalities, the BCPIIL/Re@HPC/GDL electrode can keep the selectivity toward CO when a higher amount of water is present in the electrolyte than the raw Re@HPC/GDL system. Our results help to understand the development of solid-state ionic liquids for enhanced CO₂RR in water-based electrolyte.

The reduction of CO₂ has become a hot topic in the scientific community. More specifically, the reduction of CO₂ *via* electrochemical means is considered a promising technology for producing added-value products from CO₂ (feedstocks) using an electric potential as a driving force.¹ The use of gas diffusion electrodes², heterogenized molecular catalysts³ at the industrial scale, and more recently, the use of ionic liquids (ILs) as electrolytes or additives, have been described as promising routes to obtain efficient, selective and stable catalytic systems due to the ability of ILs to efficiently solubilize and activate CO₂.^{4–6} Indeed, imidazolium-based ionic liquids have been shown to decrease the overpotential needed to drive the CO₂ reduction reaction (CO₂RR) process, likely lowering the energy of the CO₂⁻ intermediate.⁷ As such, Huan *et al.*⁸ described a copper dendrites-based electrode for CO₂RR, which showed high selectivity for formic acid (85%) at a lower overpotential in a water/ionic liquid electrolyte blend, while that system yielded mostly hydrogen in a purely aqueous medium.⁸ The shift in selectivity was attributed to the ability of ionic liquids to solubilize and activate CO₂ to such a point as to force the reaction towards the formation of formic acid, which is usually unexpected from a copper-based catalyst.^{7,8} Similarly, the presence of a small fraction of water in an ionic liquid

electrolyte was also shown to lead to hydrogen production when using a hierarchical porous carbon material (HPC) with an immobilized Rhenium-based molecular complex.⁹ The cost associated with the use of ILs has led to the development of immobilized ILs analogues. As such, polymers able to stabilize molecular catalysts in the solid-state and maximize catalyst specificity for the CO₂RR over the hydrogen evolution reaction (HER) have recently appeared in the literature.

For example, McNicholas *et al.* developed a triblock copolymer made of PS-*b*-PEO-*b*-PS (PS: hydrophobic Polystyrene; PEO: hydrophilic PolyEthyleneOxide) with an embedded 1-butyl-3-methyl imidazolium/trifluoromethanesulfonimide (TFSI) IL and a Re-based molecular complex.¹⁰ The gel obtained shows a good diffusion coefficient of electroactive species and increased specificity for the CO₂RR.¹⁰ Recently, the latter group described a polymer ion gel (PIG) using the same Re-based molecular complex including the ionic liquids in the PIG. In this case, the water-based system catalyze the CO₂RR under the same conditions as in non-aqueous solutions.¹¹ Finally, Koshy *et al.*¹² developed an IL-based ionomer able to modify the micro-environment at the catalyst-electrolyte interface and improve the catalytic performance. A silver electrode was used as a catalyst for the CO₂RR, and the effect of the imidazolium-based ionomer, deposited as a thin film on top of the catalyst, was studied. They showed that the ionomer had a strong impact on the HER competing reaction.

Herein, we report a novel functional polymer overlayer deposited atop an heterogenous catalytic system based on a molecular Rhenium catalyst immobilized on conductive hierarchically MOF-derived porous carbon material⁹ (Fig. 1). This functional layer is based on a block copolymer as a Block CoPoly(Ionic Liquid) BCPIIL, *i.e.* polystyrene-block-poly(vinyl-benzyl imidazolium) (PS-*b*-PVBIm) with a butyl-substituted imidazolium and trifluoromethanesulfonimide (TFSI) as counter-ion (Fig. 1). This functional layer is based on a block copolymer as a Block CoPoly(Ionic Liquid) BCPIIL, *i.e.* polystyrene-block-poly(vinyl-benzyl imidazolium) (PS-*b*-PVBIm) with a butyl-substituted imidazolium and trifluoromethanesulfonimide (TFSI) as counter-ion (Fig. 1). The design of the macromolecules was done to assure the polymer stacking on the conductive electrode but also the ionic liquids functionalities to boost the CO₂RR.

Indeed, the PS block was chosen for its ability to stack with the

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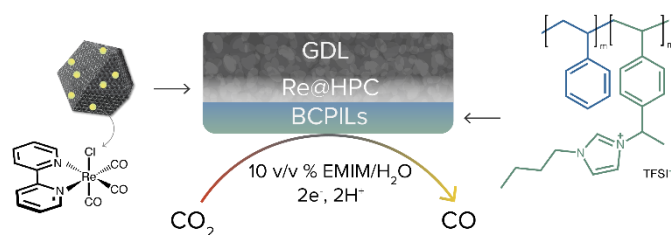


Figure 1. Schematic representation of the strategy followed in the present report.

aromatic carbon moieties of the carbon particles through Van der Waals and π - π interactions and confer hydrophobicity to the system to improve the CO₂RR.¹³ The imidazolium groups on the second block confer properties from the IL to the polymer film, *i.e.* a strong affinity with the CO₂ solubilized in the electrolyte and its activation. First, we report the synthesis by controlled radical polymerization, the subsequent functionalization, the complete polymers characterization and then the design of the complete electrodes is described, PS-*b*-PVBBI TFSI/Re@HPC/GDL. The BCPIl shows narrow Mw distribution, and no presence of monomer and impurities were found on the ¹H NMR. The BCPIls was successfully and uniformly casted on the top of the electrode and its electrochemical stability was proven under reducing conditions. Finally, the electrocatalytic activity and the selectivity of the CO₂RR were assessed in different media to investigate **the water** contents in the electrolyte, if compared with the Re@HPC/GDL previously reported.⁹

The synthesis of the PS-*b*-PIls copolymers was based on a previously reported route, in which a PS-*b*-PVBC polymer is first synthesized (target Mn 30KDa), and the chlorine atom is further substituted by an imidazole to obtain the block copoly(ionic liquids) BCPIls (Fig. 2 and Scheme S1 and S2). This post-functionalization route allows maintaining the structural integrity of the imidazolium moiety, whose stability was expected to be limited under the free-radical polymerization conditions. Consequently, a 29Kda (by SEC, see supporting information, SI) polystyrene-*block*-poly(vinylbenzylchloride) PS-*b*-PVBC was synthesized by nitroxide-mediated polymerization (NMP) as reported in the literature (see SI).^{14, 16} This polymer precursor was subsequently modified using two different imidazole precursors, 1-Ethylimidazole and 1-Butylimidazole, to obtain fully substituted BCPIls: PS-*b*-PVBEI and PS-*b*-PVBBI, respectively.

For both imidazole groups, the substitution was shown to be quantitative by ¹H NMR from the integration of the peaks at 4.5 and 5.5 ppm, arising, respectively, from the -CH₂Cl protons from the starting material and the -CH₂NR from the reaction product (Fig. 2). A quantitative substitution was deemed essential for our application to avoid the possible reduction of the chlorine atom under the conditions of the CO₂RR, as previously reported.¹⁵ The final molar masses (Fig. 2 and Table S1) of the BCPIls were calculated by ¹H NMR considering the molar mass of the initial PS-*b*-PVBC and assuming quantitative substitution of the chlorine atom. The functionalization of the PS-*b*-PVBC with the imidazole groups leads to a positive charge conjugated among the two nitrogen atoms of the imidazole ring. Upon substitution, the original benzylic chlorine atom remains in the

form of a chloride counter-ion in the polymer. In the last synthetic step, it was substituted with a bis-triflimide (TFSI) since ILs and PILs with fluorinated counter-ion have been shown to facilitate CO₂ solubility and activation (Fig. 1).⁸⁻¹¹ This exchange was followed by ¹H NMR, as shown in Fig. 2, with a shift of the proton in α or β of the nitrogen atoms. This shift proves the interaction and the influence of the counter-ion on the imidazolium ring, as previously observed by Ji *et al.*^{16,17} The molar mass of the final polymer PS-*b*-PVBEI TFSI was calculated to be 102 kDa. As mentioned above, the length of the alkyl chain on the imidazole moiety was varied to study their influence on the physicochemical characteristics of the polymers. However, the PS-*b*-PVBEI TFSI could not be isolated since the chloride counter-ion polymer precursor (Fig. S5) presented a very low solubility in the usual reaction solvents. In the case of the butyl analogue, the longer alkyl chain showed to drastically increase its solubility in organic solvents.

A BCPIls/GDL electrode was first prepared without any catalyst (see SI). Methanol and ethanol, 'good' solvents for the block copolymers, were used to dissolve PS-*b*-PVBBI TFSI before being deposited on top of the electrode. The electrodes were prepared by depositing the BCPIls on a 1 cm² commercial GDL by dip-coating and were characterized *via* controlled potential electrolysis showing stability in terms of current density for over one hour. For comparison purposes, we evaluated the stability of the BCPIls/GDL under reductive potentials in 0.5 M KHCO₃ and in 5/95 v/v H₂O/EMIM-BF₄ (EMIM). The aqueous media represent the 'best-case' scenario electrolyte while the latter medium was used in our previous work⁹, and is the starting point of this study, with the objective of reducing the EMIM content. The BCPIl/Re@HPC/GDL electrode, where a Re-based molecular complex is immobilized on the pores of hierarchical porous carbon nanoparticles (Re@HPC) was prepared (Fig. 3a).⁹ First, the supported catalyst Re@HPC was mixed with Nafion and ethanol to form a slurry that was cast on the GDL. The Re@HPC/GDL electrode was then immersed in a 2 wt% solution of the PS-*b*-PVBBI TFSI in MeOH, maintaining specific parameters of dip-coating constant (see SI), only varying the speed of substrate withdrawal. A speed of 10 000 $\mu\text{m}\cdot\text{sec}^{-1}$ was adopted for the coating as it allowed forming layers with thickness below 500 nm, as expected from the theoretical equation (Equations S4) in the SI. TGA analyses were performed (25 to 600 °C) under N₂ flow (Fig. S7) to investigate the precise amount of BCPIls present on the surface of the Re@HPC/GDL electrode (Table S2). BCPIls weight percentage loss obtained by TGA analysis show between 1.6 to 1.9 % of immobilized polymer on the GDL, corresponding to a thickness of around 250 nm which is estimated considering a flat surface and a compact layer of polymer on both sides of the electrodes. The different layers can clearly be seen in the SEM image in Fig. 3b. After the synthesis of the BCPIls and deposition on top of the GDLs, the hybrid BCPIls/Re@HPC/GDL electrodes were tested under CO₂ electroreduction conditions. Different v/v ratios of H₂O/EMIM-BF₄ were tested, namely 5/95, 10/90, 25/75 and 50/50, as an electrolyte, to assess the efficiency of the polymer layer in favoring the CO₂RR over the HER.

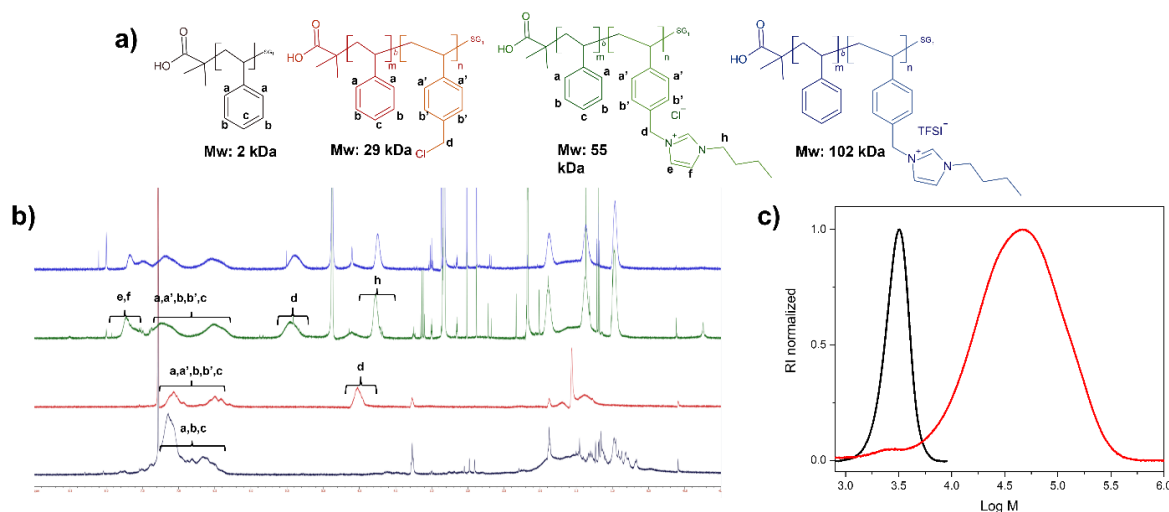


Figure 2. ^1H NMR of the purified PS block (dark blue line), purified PS-*b*-PVBC (red line), PS-*b*-PVBBI Cl (green line) macromolecules and PS-*b*-PVBBI TFSI (light blue line); the green and the light blue spectra have the same protons attribution with the corresponding letter on the molecules.

The bare Re@HPC/GDL reproduced from our previous work,⁹ and the PS-*b*-PVBBI TFSI/Re@HPC/GDL electrodes were compared.

First of all, a control experiment was carried out using a 5/95 ratio as a benchmark, however adding the BCPIs on the hybrid electrode. With the BCPIs, a decrease in current density was noted, but the selectivity for CO was kept at $-1.75\text{ V vs Fc/Fc}^+$ (Fig. S8).

The screening was then first carried out *via* linear sweep voltammetry (LSV) of the hybrid electrode in 50 % H_2O saturated with either N_2 or CO_2 (Fig. S9b). A catalytic wave at an onset potential of -1.45 V with a steady current increase up to -2.00 V (*vs Fc/Fc*⁺) applied potential was observed only in the presence of CO_2 and was thus assigned to CO_2 reduction. However, preliminary quantification using GC showed that a rather large amount of H_2 was produced (1:5 for $\text{CO}:\text{H}_2$), likely due to a large number of protons present in solution leading to enhanced H_2 production. These less-than-optimum results led us to investigate the behavior of the PS-*b*-PVBBI TFSI/Re@HPC/GDL system at lower water concentrations, therefore, 25 and 10 v/v % of H_2O in EMIM were thus tested. Using the 25 % H_2O electrolyte, a significant decrease in current density was observed at all the potentials tested compared with the 50 % H_2O concentration (Fig. S9a). This result is in line with previous work reporting an increase of current density with a higher amount of water in $\text{H}_2\text{O}/\text{ILs}$ system,^{8,9} though with less selectivity for CO_2 reduction products. In 10 % H_2O , the LSVs of the electrode in N_2 or CO_2 -saturated (Fig. 4a) showed a catalytic wave at an onset potential of -1.65 V (*vs Fc/Fc*⁺) with a steady current increase up to -2.00 V applied potential only in the presence of CO_2 ; thus, assigned to CO_2 reduction. Moreover, the catalytic wave aligns with the LSV of the Re@HPC/GDL electrode previously reported at 5 % H_2O .⁹ Under reduction potentials more cathodic than -2.00 V , the wave is present also in N_2 , being attributed to proton reduction to H_2 .

Controlled Potential Electrolysis (CPE) at different potentials was carried out coupled with quantification of CO_2 reduction products for more than 10 min to characterize the selectivity of

the CO_2RR . A higher amount of water in the electrolyte leads to higher total current density under identical applied potentials. In Figure 4b, we report the ratio of the moles of CO vs the sum of CO and H_2 moles produced with the Re@HPC/GDL and the PS-*b*-PVBBI TFSI/Re@HPC/GDL in the different electrolyte blends tested. Interestingly, at $-1.85\text{ V vs Fc/Fc}^+$, only CO is detected (TON_{CO} 2,1, TOF_{CO} 0.003 s⁻¹ see Table S4) as the gaseous product (Fig. 4b) when a 10 % H_2O electrolyte blend is used. The comparison of these results with previous work using Re@HPC/GDL electrode in the same electrolyte where only 47% FE for CO (Table S3) was detected strongly suggests that the PS-*b*-PVBBI TFSI BCPI has a significant impact on the CO_2RR specificity over the HER. Indeed, the electrode clearly shows the ability to totally suppress HER in 10 v/v % of $\text{H}_2\text{O}/\text{EMIM}$. At higher water concentrations, the selectivity decreases drastically while current density increases, as previously reported with the Re@HPC/GDL electrode.

This enhancement in CO production is undoubtedly due to the presence of the BCPI layer, which likely activates CO_2 and alters the local environment at the imidazolium polymer-hybrid active

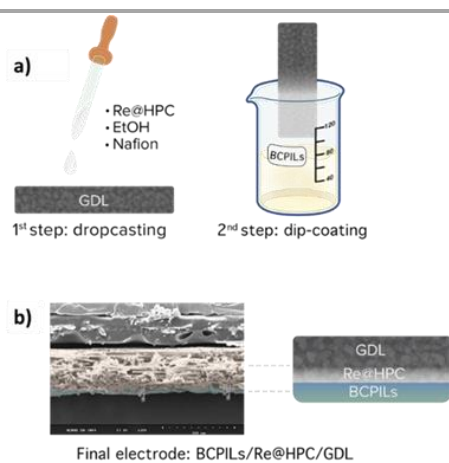


Figure 3. a) Preparation of Re@HPC/GDL and BCPIs/Re@HPC/GDL electrodes. b) cross-section SEM images of 2 wt% in MeOH PS-*b*-PVBBI TFSI /Re@HPC/GDL electrode dip-coated at $10000\text{ }\mu\text{m}\cdot\text{sec}^{-1}$.

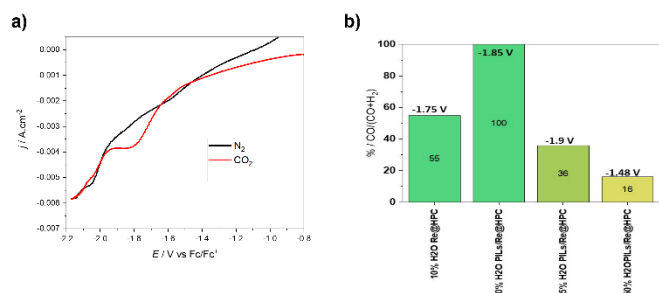


Figure 4. Controlled potential electrolysis of CO₂ using the PS-*b*-PVBBTFSI/Re@HPC/GDL electrode: a) LSV in 10% v/v H₂O/EMIM saturated with CO₂ (red) or with N₂ (black), scan rate 20 mV.s⁻¹; b) Percentage of CO/(CO+H₂) ratio for different electrodes tested at the best potential screened reported vs Fc/Fc⁺ in H₂O/EMIM

carbon interface. However, a higher potential is needed to drive the reaction forward; this is likely due to the reduced electrode surface area from the presence of the thick polymer layer. Unfortunately, the total FEs in all the cases (Table S3) where the BCPIs are employed were low likely due to the low current working regimes. Finally, CPE was carried out for 5 hours at -1.85 V. The system proved high stability in terms of current density (Fig. S10). Despite the good current density, the selectivity for CO decreases by 40% during the first 2 hours CPE, (Table S3) however no further decrease is recorded afterwards. Furthermore, post-electrolysis characterization of the electrode by SEM shows the integrity of the BCPI after 5 hours electrolysis (Fig. S11).

In conclusion, the results presented above shows that the block copolymer ionic liquid BCPI we have designed, is able to improve the selectivity of the CO₂ electroreduction to CO in aqueous/ionic liquids media when added to a Re-supported catalyst electrode. To the best of our knowledge, this is the first example of a heterogenized molecular complex for CO₂ reduction catalysis boosted by a solid-state layer of BCPI. The BCPI synthesis was performed *via* controlled radical polymerization and nucleophilic post-substitution to introduce imidazole moieties. The PIL functionalities allow to keep the selectivity toward CO when a higher amount of water is present in the electrolyte than the bare system without the BCPI. Indeed, compared to our previous work,⁹ the PS-*b*-PVBBTFSI/Re@HPC/GDL electrode clearly shows significant improvements in selectivity for CO₂ reduction to CO with stable current density. The combination of a water/ionic liquid electrolyte system and the stacked BCPIs on the electrode, along with the hierarchical porosity and efficient active sites immobilization of the Re@HPC/GDL, explain the enhanced performance of the novel system. However, as explained before, the system comprising the BCPIs suffers from lower current density than the Re@HPC. Further investigations are needed to optimize the BCPIs deposition and the layer thickness or porosity; indeed, the presence of the thick polymer layer is expected to greatly limit the kinetics of CO₂ diffusion to the catalytic center. Studies are currently underway for coupling BCPIs with electrodes whose mechanism and properties for CO₂RR are fully described in the literature. We are confident that these works will pave the way of implementing BCPIs in a

flow-cell design CO₂ electrolyzers to have more efficient CO₂RR and HER suppression and scale-up the technology.

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Conflicts of interest

"There are no conflicts to declare".

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