Editorial

Ionic Liquids for CO₂ Capture and ReductionMałgorzata E. Zakrzewska ^{1,2}

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As pointed out in the description of this thematic issue of *C*, with the current atmospheric levels of carbon dioxide being above 400 ppm, there is a growing interest in recycling this greenhouse gas in the form of valuable compounds. The abundance of carbon dioxide is undoubtedly one of the biggest issues of our times, but it can also be a remarkable opportunity for the production of carbon-based fuels, materials and chemicals. Many efforts are being made globally, in both academia and industry, to increase the small contribution of Carbon Capture and Utilization (CCU) technologies to long-term climate mitigation. The reduction of CO₂ to energetic compounds, such as carbon monoxide, formic acid, methanol, methane and other hydrocarbons, is of key importance for decreasing our dependency on fossil fuels.

Ionic liquids consist of ionic species, a bulky organic cation weakly coordinated to either an organic or an inorganic anion. It is this weak coordination and asymmetry of ions that results in a reduction in the lattice energy and crystalline structure of ionic liquid, lowering its melting point. What makes these innovative fluids even more special, is that their structure can be easily tailored by changing cation/anion combinations and/or by attaching functional groups. Consequently, physicochemical properties can be optimised according to the requirements of the intended use. Research into ionic liquids has undergone an exponential growth in the last two decades, and, as an environmentally more acceptable alternative to volatile organic solvents, ionic liquids have found their way into a wide variety of industrial applications. Of course, in order to make any process at a large scale, a security of supply and cost must be assured. However, being designer solvents, ionic liquids can be based on ions falling within an available (wide) price range. Additionally, recycling and reuse of the ionic liquids due to their negligible vapour pressure can be facilitated, further minimising the relevance of the initial cost.

In the first article of this thematic collection, Ibram Ganesh [1] proposed a simple and straightforward route for the synthesis of high-purity 1-butyl-3-methylimidazolium tetrafluoroborate (bmim[BF₄]), using locally available and inexpensive starting materials, namely n-bromobutane and 1-methylimidazole. The synthesised ionic liquid was evaluated as a helper catalyst/mediator to promote the electrochemical carbon dioxide reduction (ECR) to carbon monoxide, over tin (Sn) and molybdenum disilicide (MoSi₂) cathodes.

Indeed, ionic liquids, being composed entirely of ions, possess a multitude of charge carriers and, as such, are a perfect choice for electrochemical applications. In fact, ionic liquids' first utilisations were as solvents in studies of solution electrochemistry, electrodeposition, and as electrolytes in electrochemical devices, i.e., semiconductors or batteries. It has been shown that ionic liquids have a wide electrochemical window, a broad range of ionic conductivity, and high thermal stability. In the ECR reaction, the function of ionic liquid has been described as mainly CO₂ absorption and assistance with CO₂^{•−} (radical anion) stabilisation. The ability of some ionic liquids to lower the overpotential for ECR was confirmed; however, the presence of viscous ionic liquid may inhibit CO₂ mass transfer into the cathode catalyst layer and cause problems with electrochemical cell stability, due to the degradation of the very same ionic liquid. In the review, Kaczur et al. [2] discussed

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the application of imidazolium-based ionic liquids tethered to polymer backbones as a way to increase the stability of an electrochemical system in ECR to carbon monoxide and formic acid.

Carboxylic acids can also be obtained through the direct carboxylation of carbon nucleophiles, using carbon dioxide as an electrophile. Mena and Guirado [3] investigated the influence of the potential applied, nature of the cathode and electrolyte used on the electrochemical valorisation of carbon dioxide. Depending on the type of organic mediator used, either a nitro or cyano aromatic derivative, the electrochemical activation of carbon dioxide can lead to various outcomes, from electrocarboxylated compounds to oxalate as main product.

Regardless of the CO₂ conversion end product type, finding a suitable method of removing it from the reaction mixture is fundamental to assuring the sustainability and competitiveness of any chemical process. The oldest and the most widely used separation operation in industry is distillation. However, apart from a high energy penalty, in case of removing compounds present in low concentrations, mixtures of components with close boiling points, or azeotropes, this conventional method is ineffective.

Lakkaraju and co-workers [4] evaluated a pervaporation technique for concentrating formic acid produced from ECR, using three distinct types of membranes (cation ion exchange, anion ion exchange, and microporous hydrophobic membranes).

Nunes and co-workers [5] investigated the possibility of performing the synthesis of levulinic acid from butanediol and carbon dioxide in a supercritical carbon dioxide–ionic liquid biphasic system. The underlying reason for such an approach is an unusual phase behaviour of the CO₂–ionic liquid biphasic system, where most ionic liquids can absorb high concentrations of carbon dioxide, while they are immeasurably insoluble in dense carbon dioxide phase. In a continuous mode of operation, the desired product can be continuously extracted with water, without any solvent cross-contamination, keeping ionic liquid with a catalyst inside the reactor for reutilisation.

In sum, by taking advantage of ionic liquid's large affinity for carbon dioxide, a plethora of possibilities exists to design ionic-liquid-mediated CO₂ valorisation processes on an industrial scale. We would like to thank all the authors for their contributions to this thematic Issue, and we hope that you enjoy reading it and feel inspired by the articles combined in this collection.

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