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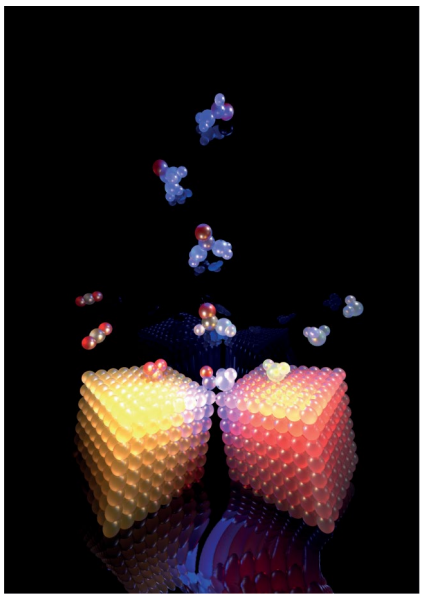
Electrosynthesis of C–X bonds from CO_2

Electrocatalytic synthesis of chemicals and fuels is seen as one way to decarbonize the chemicals industry. In this focus issue, we examine the electrochemical coupling of CO_2 with heteroatoms for sustainable chemical synthesis.

The synthesis of fuels and chemicals relies heavily on fossil fuel resources, for energy input and raw materials. Chemical manufacturing accounts for 37% of the greenhouse gas emissions from industrial processes[1]. Electrochemical production of chemicals is considered a greener synthetic route as the required energy input can come from electricity generated from renewable sources, and waste products can be used as chemical building blocks. In particular, the use of CO_2 as a building block for chemicals and fuels is attractive, as CO_2 can be removed from the air and converted into value-added products, reducing emissions, and closing the carbon cycle[2]. Pilot plants for electrocatalytic CO_2 reduction (CO_2R) to form small carbon, hydrogen and oxygen containing molecules, are already being tested[3]. However, many high-value industrially produced chemicals contain other heteroatoms such as nitrogen, sulfur and phosphorus.

The scope of products that can be generated from abundant building blocks such as CO_2 has therefore been expanded to molecules containing C–N, C–S, and C–P bonds through co-reaction of heteroatom-based small molecules during CO_2R. Whilst the co-reaction of N-containing molecules is most commonly discussed, possibly due to C–N-bond-containing products having the largest market value, there are also recent examples of co-reaction with S- and P-containing reagents[4]. In a Review in this issue, Dinh, Seifitokaldani, Kornienko and co-authors discuss reactions that use CO_2 and abundant heteroatom-containing reagents as building blocks for electrifying the synthesis of C–X-bond-containing products. The reactions using CO_2 as a building block are categorized into (1) surface–solution coupling, (2) co-reduction and (3) near-surface



coupling, and the catalysts, reactors and reactivity that enable the coupling pathways are discussed. The Review highlights — as a common theme in electrocatalysis — the need for establishing a standard set of performance metrics for benchmarking as the field grows.

In a Comment in this issue, Wang and Rooney discuss electrocatalytic methylation and amination reactions for the sustainable electrosynthesis of organonitrogen compounds from CO_2 or NO_x^{y-}. Whilst the electrochemical reduction of CO_2 or NO_x^{y-} have been extensively studied in the past decade, there are few examples of the application of these reactions for chemical coupling to methyl and amino functionalities. They examine the opportunities and challenges of electrocatalytic methylation and amination reactions, suggesting that the development of electrocatalysts with specific reactivities is necessary for future work.

In a Q&A with Marta Costa Figueiredo we learn about the challenges of co-reducing CO_2 with NO_3^-, owing to the stability of the CO_2 molecule and the slow rate of NO_3^- reduction. Both reduction reactions need to be optimized to achieve high performance of the electrocatalyst. For state-of-the-art optimized catalysts, however, activities and selectivity remain low and the scalability of the reaction at industrial-scale is challenging. Zhang, Liu and Gao discuss the need for multidisciplinary research in organonitrogen electrosynthesis in a Comment. More specifically, the role and importance of the selectivity of the catalyst towards key intermediates, the interface microenvironment where the catalysis typically occurs and the rational design of electrochemical reactors, amongst other factors, are considered for electrocatalytic C–N formation.

Whilst turning waste CO_2 into chemical feedstocks through co-reduction with heteroatom-based molecules is attractive as a sustainable synthetic route, there are other considerations to be made. These are discussed by Jennifer Dunn in a World View in this issue. Ideally, waste CO_2 should be used for the CO_2R, and it should be coupled with waste sources of heteroatoms. However, these processes may require complex, energy-intensive and costly purification steps, due to the high levels of impurities in waste sources. For electrocatalysis at scale, electrolysers must be used, and these contain precious or rare metals as the electrocatalysts, which are often mined at huge ecological expense. The source of electricity to drive the electrocatalysis is also a question, and Dunn makes us think about how difficult this can be to trace and about which use of "green electrons" is most justified.

The co-reaction of heteroatom-containing chemicals during CO_2R is a promising route for the green synthesis of chemical feedstocks and fuels. This has been a rapidly expanding area of research in the past decade and is only likely to grow as the chemicals industry moves away from petrochemical-based operations. However, as seen in the articles in this issue, there are many questions that should be considered when using electroreduction as an alternative synthetic method.

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