Carbon dioxide electrotransformation into value-added chemicals in ionic liquid-based electrolytes
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(a) Cyclic voltammetry curves for CO$_2$ reduction on carbon film electrode and metal-free carbon nanofibres (CNFs) electrode. (b) Absolute current density for CO$_2$ reduction at different electrodes in pure [Emim]BF$_4$ electrolyte. (c) Current density for CNFs catalyst with respect to H$_2$O mole fraction (%) in [Emim]BF$_4$. (d) Chronoamperogram for CNFs catalyst in pure [Emim]BF$_4$. (e) Proposed schematic diagram for CO$_2$ reduction mechanism. Credit: Science China Press

The use of fossil fuels as energy carriers and raw materials promotes the rapid development of society. However, the excessive exploitation of fossil fuels has given rise to an energy crisis and undesirable environmental changes. In particular, a continuous increase of CO$_2$ concentration in the atmosphere, which is > 400 ppm today and is estimated to triple by 2040, might result in a series of environmental issues, such as global warming, rising sea levels, and more extreme weather. Therefore, cutting CO$_2$ emissions and developing abundant renewable energy are urgent needs and challenges for our society.

CO$_2$ is not only one of the main greenhouse gases but also an abundant, nontoxic, nonflammable, and renewable C1 resource. Electrochemical conversion of CO$_2$ is an attractive way to recycle CO$_2$ into value-added products and make it possible to store electrical energy in chemical form. As an important component in the electrocatalysis process, the electrolyte interacts with the electrode surfaces, reactants, and intermediates, which plays a key role in charge transport. Different electrolytes have been explored to promote the development of CO$_2$ electrochemical conversion technology.

Ionic liquids (ILs) are organic salts composed of cations and anions with the melting point below 100 C. Many of them are liquids even at room temperature. ILs have been demonstrated to be the very promising candidate electrolytes for the electrochemical conversion of CO$_2$ due to their unique structural features and physical properties, e.g., high absorption capacity of CO$_2$, high intrinsic ionic conductivity, and wide electrochemical potential widows.

In a new overview published in the Beijing-based National Science Review, scientists at the Institute of Chemistry, Chinese Academy of Sciences in Beijing, China present the latest advances in electrochemical transformation of CO$_2$ into value-added chemicals in IL-based electrolytes. Co-authors Xingxing Tan, Xiaofu Sun, and Buxing Han trace the history of the development of CO$_2$ electrochemical transformation in IL-based electrolytes; they also review representative ILs system, electrocatalysts, and reactor configurations used in CO$_2$ electrochemical transformation.

These scientists likewise outline the potential development directions of IL-based electrolytes for CO$_2$ electrochemical transformation.

"Typically, CO$_2$ electroreduction (CO$_2$ER) and CO$_2$ electroorganic transformation (CO$_2$EOT) are two important routes to convert CO$_2$ into value-added carbonic fuels and chemicals. CO$_2$ electroreduction
represents an essential approach for CO₂ utilization, in which CO₂ could be transformed into many platform chemicals through the construction of C-H bond, such as hydrocarbons, acids, and alcohols. In addition, CO₂ can be used as one of the reactants to react with different substrates (e.g., alkenes, alkynes, ketones, epoxides, aziridines, or propargylic amines) to synthesize carboxylic acids, cyclic carbonates, and oxazolidinone derivatives through the construction of C-C, C-O, or C-N bonds," they state in an article titled "Ionic Liquid-Based Electrolytes for CO₂ Electroreduction and CO₂ Electroorganic Transformation."

"The typical system for CO₂ER consists of anode and cathode compartments separated by a proton exchange membrane. Both CO₂ reduction reaction and HER take place at the cathode driven by electric energy over the catalyst. CO₂EOT is usually performed in undivided cells," they add. "The electrolyte undertakes the role of transporting charge species. Studies have demonstrated that ILs could reduce the initial barrier of CO₂ conversion through lowering the formation energy of CO₂ - intermediate. Moreover, the competing hydrogen evolution reaction (HER) could be suppressed in the presence of ILs, which might be favorable to improving the selectivity of CO₂ conversion."

Syngas was obtained by electrolyzing supercritical CO₂ and water in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF₆) electrolyte in 2004. The reduction of CO₂ to CO with a Faradaic efficiency (FE) of 96% was achieved in an electrocatalytic system with Ag cathode and 18 mol % 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄) solution electrolyte in 2011, which was marked as an important breakthrough in the development of IL electrolytes for CO₂ER.

DMC is almost the most studied product of CO₂EOT that involve the use of ILs. "Electrocatalytic fixation of CO₂ to epoxides or alcohols to yield organic carbonates via C-O bond formation can avoid the use of toxic phosgene or CO₂, providing a green and atom economy pathway for the synthesis of organic carbonates," they state.

"Further improvement in the performance of electrochemical conversion of CO₂ can be achieved by designing novel functional IL-based electrolytes and exploring innovative electrocatalysts and optimized electrode/reactor configurations. It will also be of great significance to use CO₂ as C1 synthon to prepare more diverse chemicals by the construction of different kinds of C-X bonds, like C-Si, C-P, C-S bonds," the scientists forecast.

"The current advancement of electrochemical transformation of CO₂ should address the large overpotential, low current density, unsatisfactory product selectivity and yield urgent, especially for value-added C2+ products," they add. "ILs are considered to offer great potential for CO₂ conversion technology. Electrochemical transformation of CO₂ in IL-based electrolyte is expected to integrate CO₂ fixation with renewable electricity storage, providing an avenue to close the anthropogenic carbon cycle."


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