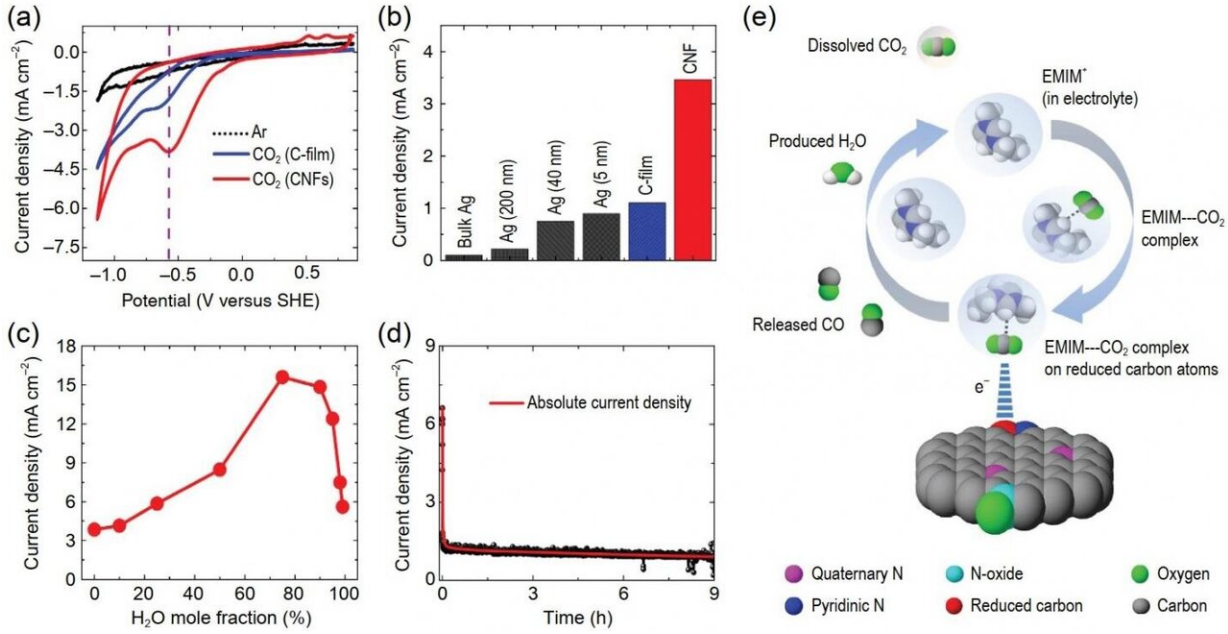
Carbon dioxide electrotransformation into value-added chemicals in ionic liquid-based electrolytes

March 17 2021



(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]BF4 electrolyte. (c) Current density for CNFs catalyst with respect to H_2O mole fraction (%) in [Emim]BF4. (d) Chronoamperogram for CNFs catalyst in pure [Emim]BF4. (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_2ER) and CO_2 electroorganic transformation (CO2EOT) are two important routes to convert CO_2 into value-added carbonic fuels and chemicals. CO_2 electroreduction represents an essential approach for CO_2 utilization, in which CO_2 could be transformed into many platform chemicals through the construction of C-H bond, such as hydrocarbons, acids, and alcohols. In addition, CO_2 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 CO_2 Electroreduction and CO_2 Electroorganic Transformation."

"The typical system for CO_2ER consists of anode and cathode compartments separated by a proton exchange membrane. Both CO_2 reduction reaction and HER take place at the cathode driven by electric energy over the catalyst. CO_2EOT 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 CO_2 conversion through lowering the formation energy of CO_2 - 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 CO_2 conversion."

Syngas was obtained by electrolyzing supercritical CO_2 and water in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF6)

electrolyte in 2004. The reduction of CO_2 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 CO_2ER.

DMC is almost the most studied product of CO2EOT that involve the use of ILs. "Electrocatalytic fixation of CO_2 to epoxides or alcohols to yield organic carbonates via C-O bond formation can avoid the use of toxic phosgene or CO, providing a green and atom economy pathway for the synthesis of organic carbonates," they state.

"Further improvement in the performance of electrochemical conversion of CO_2 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 CO_2 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 CO_2 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 CO_2 conversion technology. Electrochemical transformation of CO_2 in IL-based electrolyte is expected to integrate CO_2 fixation with renewable electricity storage, providing an avenue to close the anthropogenic carbon cycle."

More information: Xingxing Tan et al, Ionic Liquid-Based electrolytes for CO_2 electroreduction and CO_2 electroorganic transformation, *National Science Review* (2021). DOI:

10.1093/nsr/nwab022