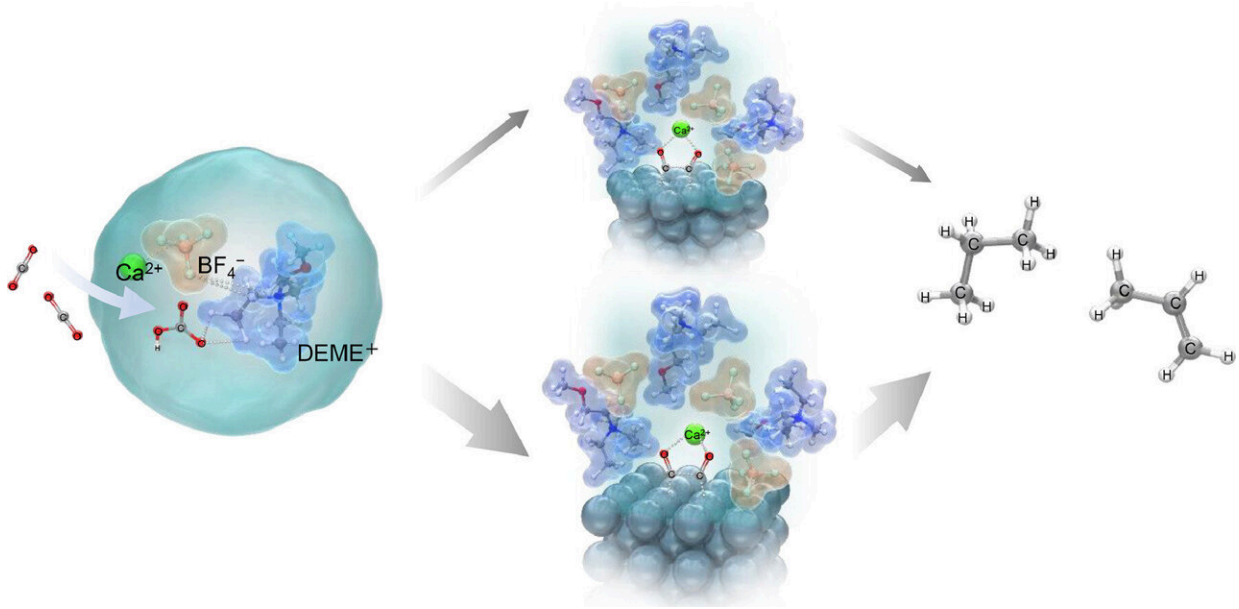
Ionic liquid electrolyte enables efficient CO_2 conversion to fuels and chemicals

June 3 2024



The production of hydrocarbons occurs through two intermediates formed on the surface of the silver electrode to produce useful hydrocarbons like ethylene, ethane, propylene, and propane. Credit: Takuya Goto / Doshisha University

Converting CO_2 into fuel and chemicals using electricity, also known as electrochemical conversion of CO_2, is a promising way to reduce emissions. This process allows us to use carbon captured from industries and the atmosphere and turn it into resources that we usually get from fossil fuels.

To advance ongoing research on efficient electrochemical conversion, scientists from Doshisha University have introduced a cost-effective method to produce valuable hydrocarbons from CO_2. The study is published in the journal *Electrochimica Acta*.

The research team, led by Professor Takuya Goto and including Ms. Saya Nozaki from the Graduate School of Science and Engineering and Dr. Yuta Suzuki from the Harris Science Research Institute, produced ethylene and propane on a basic silver (Ag) electrode by utilizing an ionic liquid containing metal hydroxides as the electrolyte.

"Most studies on CO_2 electrolysis with room-temperature liquid electrolyte have focused on the electrode's catalytic properties. In this groundbreaking study, we focused on the electrolyte and succeeded in producing valuable hydrocarbon gas even on a simple metal electrode," says Prof. Goto.

Ionic liquids offer unique advantages for the electrochemical reduction of CO_2. They operate over a wide range of voltages without decomposing, are non-flammable, and have high boiling points. This stability enables the electrolyte to withstand the high temperatures generated during exothermic CO_2 reduction.

In their study, researchers investigated the electrochemical conversion of CO_2 and water with N, N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate (DEME-BF_4) as the electrolyte.

The DEME-BF_4 electrolyte provides optimal conditions for maximizing CO_2 reduction. $DEME^+$ ions enhance the solubility of CO_2, allowing a greater number of CO_2 molecules to participate in the reaction. Moreover, due to its hydrophilic nature, the hydrogen ions required for reducing CO_2 to hydrocarbons can be easily supplied by mixing the electrolyte with water.

The researchers determined that the electrochemical conversion of CO_2 to hydrocarbons could be increased with the addition of aqueous solutions containing metal hydroxides like calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH), and cesium hydroxide (CsOH) to the electrolyte.

The hydroxides in the ionic liquid can react with CO_2 to form bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}), further enhancing the availability of CO_2 to participate in electrochemical reactions.

Under room temperature electrolysis (298 K or 25°C) in a CO_2 atmosphere, the researchers successfully reduced CO_2 to ethylene (C_2H_4), ethane (C_2H_6), propylene (C_3H_6), and propane (C_3H_8).

They achieved the highest current efficiencies for each product using DEME-BF_4 electrolyte mixed with water and containing $Ca(OH)_2$, with efficiencies reaching up to 11.3% for propane and 6.49% for ethylene. This efficiency surpassed those obtained with other metal hydroxides by over 1,000 times.

The reason for this high efficiency was explained using Raman spectroscopy and density functional theory (DFT) calculations. These analyses revealed that bicarbonate ions, formed when CO_2 interacts with OH^- ions in the electrolyte, interact with $DEME^+$ and BF_4^- ions of the electrolyte to form a stable structure [$DEME^+$-BF_4^--HCO_3^--Ca^{2+}].

CO_2 and HCO_3^- species then adsorb onto the electrode surface forming adsorbed species CO^-_{ads}. The adsorbed CO^- ions then strongly interact with Ca^{2+} ions present in the electrolyte, forming two distinct intermediate structures: One structure A, consisting of a Ca^{2+} ion coordinated with two CO^- ions adsorbed on three Ag atoms, and the other Structure B, where the Ca^{2+} ion is coordinated with two CO^- ions adsorbed on two Ag atoms.

This interaction with Ca^{2+} ions is crucial as it increases the stability of the adsorbed species, making the subsequent electrochemical reactions possible.

Among these structures, researchers suggest that structure B is more stable and is the preferred pathway for ethylene, while structure A leads to the production of propane.

"We showed that tailoring the electrolyte can lead to molecular-level changes in the phase transformation of CO_2 in bulk solution and at the electrode/ionic liquid electrolyte interface and proposed a process that enables the synthesis of unique hydrocarbons such as C_3," says Prof. Goto.

These findings shed light on the processes involved in the conversion of CO_2 at the interface between ionic liquid-based electrolytes and metal electrodes, such as the role of calcium ions. Such insights can help in the development of electrolytes for the efficient production of useful hydrocarbons from CO_2.

"The physicochemical knowledge of this new route from CO_2 decomposition to synthesizing useful hydrocarbons, as revealed in this study, will be instrumental in advancing CO_2 utilization technology and contributing to academic progress in materials science," concludes Prof. Goto.

More information: Saya Nozaki et al, Electrochemical synthesis of C2 and C3 hydrocarbons from CO_2 on an Ag electrode in DEME-BF4 containing H_2O and metal hydroxides, *Electrochimica Acta* (2024). DOI: 10.1016/j.electacta.2024.144431

Provided by Doshisha University