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Electrochemical reduction of carbon dioxide at low overpotential on a polyaniline/Cu_2O nanocomposite based electrode

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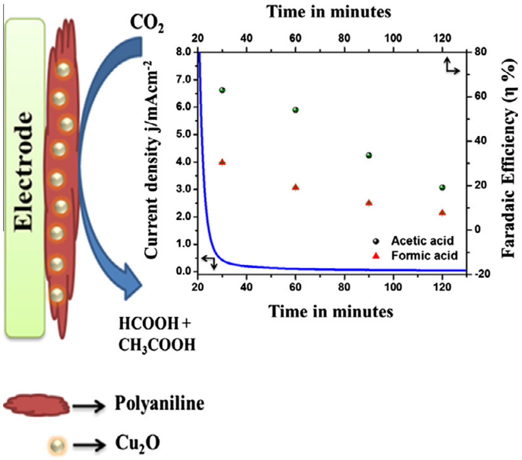
HIGHLIGHTS

- Potentiostatic and current deposition technique was used to fabricate electrodes.
- Cu_2O dispersed polyaniline electrodes was fabricated.
- CO_2 was reduced by potential electrolysis method at different potentials.
- A faradaic efficiency of 30.4% and 63.0% HCOOH & CH_3COOH was observed at −0.3 V.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrochemical reduction of CO_2 using Cu_2O nanoparticle decorated polyaniline matrix (PANI/Cu_2O) in 0.1 M tetrabutylammonium perchlorate (TBAP) and methanol electrolyte was investigated under ambient conditions. The experiment was carried out in a divided H-type two-compartment cell with a Nafion membrane as diaphragm separating the cathodic and anodic compartments. The catalyst was synthesized electrochemically as a thin film by using cyclic voltammetry and constant current mode deposition technique. The as-fabricated electrode was analyzed with various techniques to probe the nature and composition of the nanoparticles deposited onto the polyaniline matrix, which confirmed the presence of well-defined Cu (I) species in the film. The reduction of CO_2 was carried out at various polarization potentials; the main products were formic and acetic acid with faradaic efficiencies of 30.4% and 63.0% at a polarization potential of −0.3 V vs. SCE (sat. KCl). A possible reduction pathway is through the formation of H_{ad} atoms and subsequent transfer to CO_2 through the polymer film to form the products. An appreciable efficiency was achieved in the formation of formic acid and acetic acid with the developed catalyst.

1. Introduction

Among the contemporary energy objectives, the reduction of carbon dioxide emission is a major issue of immediate concern.

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Anthropogenic CO_2 in the atmosphere is claimed to be the major contributor to the greenhouse effect, and the immediate consequence is the phenomenon of global warming [1–3]. The famous Keeling curve shows an annual rise of 1.9 ppm per year [4]. The Intergovernmental Panel on Climate Change (IPCC) has predicted that levels of CO_2 could reach 730–1020 ppm by 2100, which would result in a mean global temperature rise of 1.4–1.9 K and ocean acidification by 0.14–0.35 pH units [5]. The adverse impacts of global warming include rising sea levels, disappearance of some islands, extreme weather, and climate change [5,6]. Therefore, reducing CO_2 emissions into the atmosphere has become a critical issue. In addition to efforts to capture and store CO_2 in the hope of reducing the greenhouse effect, the conversion of CO_2 to fuels and chemical feedstock is an attractive proposition that could provide an alternative solution to both the current energy crisis and climate issues [7–9]. Various methods have been developed to reduce CO_2 emissions, such as chemical, thermochemical, photochemical, electrochemical, and biochemical techniques [10–12]. Of these methods, electrochemical reduction is simple and can be performed under ambient conditions, and is of particular interest since it could both mitigate greenhouse gas emission and use CO_2 as a carbon source to produce a variety of fuels such as formic acid and methanol [12–16]. The intermittency of renewable energy sources requires practical energy storage solutions. This can be accomplished by finding an efficient way to store energy in the form of chemical fuels, which would be particularly appealing if combined with CO_2 capture [17,18]. Thus the electrochemical reduction of CO_2 using renewable sources of electricity is an alternative approach to the production of fuels, akin to photosynthesis, which could potentially reduce the dependence on fossil fuels and mitigate CO_2 emissions into the atmosphere [19]. The electrocatalytic reduction of CO_2 to fuels is thus a critical goal that would positively impact the global carbon balance [20–22]. However, CO_2 is an extremely stable molecule, so the conversion of CO_2 to a useful fuel on the same scale as its current production is beyond our present scientific and technological abilities [7].

In addition, the direct electrochemical reduction of CO_2 needs at least 1–2 V of overpotential. The conversions of CO_2 to formic acid, methane, ethane, ethylene, propylene, oxalic acid, methanol, and ethanol have been reported under various electrocatalytic conditions and in various solvents [23,24]. Of the useful chemicals into which CO_2 can be electrochemically converted, formic acid appears to offer the most promise for the practical development of technical and economical viable processes. Traditional industries use formic acid in silage preservation, as an additive in animal feeds, in textile finishing, and as a chemical intermediate [25]. Moreover, formic acid offers easy transport and storage and is one of the most promising candidate fuels for low-temperature fuel cells [26]. However, the manufacture of formic acid is relatively expensive and has negative environmental impacts [27,28]. Thus more attention has been paid to the electrochemical reduction of CO_2 to formic acid in recent years [29–31]. The electrochemical reduction of CO_2 to formic acid is described by the following equation:

$$CO_2 + 2H^+ + e^- \rightarrow HCOOH \tag{1}$$

The theoretical potential for the electrochemical reduction of CO_2 to formic acid under standard conditions is −0.854 V (SCE, sat. KCl) [30]. As a result of the high overpotential, a voltage of more than 4 V is required to decrease the cathode potential of any common metal electrode to below −1.545 V (SCE, sat. KCl) for effective CO_2 reduction. Thus the development of new catalysts is crucial if we are to reduce this overpotential and create an efficient electroreduction process.

Many investigators have studied the electrochemical reduction of CO_2 using various metal electrodes in organic solvents, given that organic aprotic solvents dissolve much more CO_2 than water [32–34]. Methanol is a better solvent of CO_2 than water and the solubility of CO_2 in methanol is approximately 5 times that in water, at ambient temperature, and 8–15 times that in water below 0 °C [35–37]. Further, if water is used as a solvent for the reduction of CO_2, hydrogen evolution decreases the current efficiency significantly. It has also been shown that the faradaic efficiencies of products from CO_2 in methanol are better than those obtained in water [38]. Many authors have reported the reduction of CO_2 in methanol as the medium [39–43].

Mediated electrocatalysis represents the catalytic effect which assumes an interaction between mediator-electrode and the substrate molecules i.e. CO_2. The advantages of this method are a decrease in the electrochemical potential at which electrochemical reductions occur and an increase in the selectivity of the process. In general, metal electrodes need a high negative potential of less than −1.7 V (SCE, sat. KCl) for the electroreduction of CO_2. To decrease this potential, new electrode materials are required. In this connection, conducting polymers such as polyaniline, polypyrrole, and polythiophene have gained recognition over the last two decades [43]. The reasons for this interest are their peculiar properties and the applications of these materials in various niche areas. A polyaniline electrode laminated with Prussian blue (consisting of a mediating inorganic conductor and polymer) has been used for CO_2 reduction under high pressure by Ogura et al. [44]. With this modified electrode, CO_2 was reduced at −0.845 V (SCE, sat. KCl) and the reaction products were lactic acid, acetic acid, formic acid, methanol, and ethanol. In another study [45,46], bulk polyaniline was used as the electrode material in the reduction of CO_2 to organics such as formaldehyde, formic acid, and acetic acid at −0.4 V (SCE, sat. KCl). Koleli et al. used polypyrrole electrodes to reduce CO_2 in a methanol/$LiClO_4$ system, which produced formic and acetic acid at an electrolysis potential of −0.445 V (SCE, sat. KCl) [47,48]. All these reports suggest that the use of conductive polymers enables the electrochemical reduction of CO_2 at lower overpotentials and produces formic acid with a good faradaic efficiency. Cu_2O is yet another fascinating material, a p-type semiconductor with a direct band gap of 2.14 eV. Cu_2O has received extensive attention in various applications because of its low cost and robust chemical nature [49]. As this material is stable in most organic and aqueous solutions, it is a promising candidate for the electrochemical reduction of CO_2.

This study tested the use of a polyaniline matrix decorated with Cu_2O nanoparticles as electrode for the electrochemical reduction of CO_2 to valuable fuels. We aimed to determine how to maintain a high current efficiency in this system and the concentration of formic acid that could be build up in the catholyte. A simple and novel electrochemical process was used for the fabrication of the working electrode. For CO_2 electroreduction, a special H-type reactor was designed, and fabricated with Nafion membrane as a separator.

2. Experimental

2.1. Reactor construction

The electroreduction of CO_2 was carried out in an H-type two-compartment cell with an anode and a cathode. The two compartments were separated by a proton exchange membrane (Nafion 117, 0.177 mm thickness) as the diaphragm. The cell was constructed of glass, with two orifices and gas purging inlet in the cathode compartment, an orifice and a gas inlet port in the anode compartment, and O-rings to hold the electrodes and membrane. The working and reference electrodes were housed in the cathode compartment and the counter electrode was mounted in the anode compartment. A schematic diagram of the electroreduction set-up