



Syngas production by electrochemical CO₂ reduction in an ionic liquid based-electrolyte



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ABSTRACT

The electrochemical reduction of carbon dioxide dissolved in a solution of water and ionic liquid as electrolyte, at high-pressure and near room-temperature, is reported. This work describes an electro-deposition strategy for the preparation of copper substrate cathodes, coated with bimetallic zinc–copper films, obtained from deep-eutectic solvents plating baths. The prepared bimetallic cathodes showed electrochemical activity for syngas production in 1-butyl-3-methylimidazolium triflate, with yields of 85 N μ L (normal microliter) cm⁻² C⁻¹/170 N μ L cm⁻² h⁻¹, high selectivities, tunable H₂/CO ratio and low energetic requirements.

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1. Introduction

In general electrochemical processes, offer good reaction selectivity and reduced cost, because of the possibility of direct control of electrode surface free energy through electrode potential. These processes are sustainable only when electricity is obtained from renewable sources. The intermittent nature of these energy sources requires the capacity for large-scale electricity storage. This work reports the development of a low temperature process (near room temperature) for producing non-fossil syngas by co-electrolysis of CO₂ and water that has the potential to achieve this goal.

Syngas is a very valuable and versatile energy carrier. It can be converted into easily stored and transported liquid fuels by the well-established Fischer-Tropsch technology [1]. It can be produced from any hydrocarbon feedstock, natural gas, naphtha, residual oil, petroleum coke, coal, and biomass. All these processes have in common the use of high temperatures, well above 100 °C. At present, syngas is mainly produced from steam reforming of natural gas. Despite this being a mature technology, processes for

syngas production using several feedstocks are being actively investigated to increase their efficiency and lower their production cost [2,3].

Electrochemical carbon dioxide reduction into chemicals, such as fuels, has been actively investigated due to its potential for converting waste CO₂ captured from industrial emissions into carbon neutral products. However, due to the extreme stability of the CO₂ molecule, the potential that is necessary to apply for CO₂ electrochemical reduction in water at 25 °C, at atmospheric pressure is high: −1.9 V vs. SHE, because the first electron reduction involves the bending of the linear CO₂ molecule to form the [^{*}CO₂]⁻ radical anion [4]. Therefore, the energy required for the process is usually high, and the energy efficiency as well as yield of the desired product are generally low [5].

Zhao et al. [6] used for the first time room temperature ionic liquids (ILs) as electrolytes for the electrochemical reduction of high-pressure CO₂, without other carbon-based reagents, due to their wide electrochemical windows, high solubility for CO₂ and reasonably good intrinsic ionic conductivities.

Room temperature ILs are generally defined as organic salts that are liquid at temperatures below 100 °C. The capability of ionic liquids to absorb CO₂ both physically [7] and chemically [8] opens-up the possibility of simultaneous capture and conversion CO₂ into valuable chemical products. Following the pioneer work of Zhao

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et al. other researchers have used ILs as an additive to the electrolyte [9,10].

In this context, Alvarez-Guerra et al. published a comprehensive review that includes the use of ILs in electrosynthesis of valuable compounds, using CO₂ as a reactant, and in the electrochemical reduction of CO₂ without other carbon-based reactants [11]. This review work clearly shows the important role of certain imidazolium-based ILs in lowering the overpotential of electrochemical CO₂ reduction. Rosen et al. [12] used a silver working electrode to reduce CO₂ to CO at atmospheric pressure in a hydrated IL 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), where water was the proton source at overpotentials as low as 0.2 V with Faradaic efficiencies higher than 96%. This study also showed that the ionic liquid lowers the energy of the [CO₂]⁻ intermediate thereby decreasing the initial barrier to reduction. Di Meglio et al. [9] have reported that an economical bismuth-based material could promote the electrochemical conversion of CO₂ to CO at overpotentials below 0.2 V operating with a Faradaic efficiency of approximately 95%. CO₂ saturated acetonitrile containing millimolar concentrations of a 1,3-dialkyl substituted imidazolium based ionic liquid promoter such as 1-butyl-3-methylimidazolium triflate ((BMIM)OTf) was used as electrolyte. Zhang et al. [13] have demonstrate the effect of Bi catalyst's size and surface condition for an efficient organic phase CO₂ conversion to CO. Medina-Ramos et al. [10] showed that electrochemically prepared Bi and Sn catalysts were highly active, selective and a robust platform for CO evolution, with partial current densities of 5–8 mA cm⁻² at applied overpotentials <0.25 V in the presence of (BMIM)OTf in acetonitrile solutions. By contrast, electrodeposited Pb and Sb catalysts do not promote rapid CO generation with the same level of selectivity. The Pb-material is only approximately 10% as active as the Sn and Bi systems at an applied potential of -1.95 V and is rapidly passivated during catalysis. Watkins et al. [14] used an aqueous solution of 1-ethyl-3-methylimidazolium trifluoroacetate (EMIMTFA) for the direct reduction of carbon dioxide into formate at indium, tin, and lead electrodes; yields of ca. 3 mg h⁻¹ cm⁻² were obtained. Product selectivity was observed upon changing the IL anion. In EMIM based ILs on Pb electrodes oxalate formation is favoured in the presence of Bis(trifluoromethylsulfonyl)imide (NTF₂), whereas formate formation is favoured when trifluoroacetate (TFA⁻) is used as referred above [15]. Barrosse-Antle et al. [8] studied CO₂ electrochemical reduction in 1-butyl-3-ethylimidazolium acetate observing that CO₂ electrochemical reduction was not sustainable, because CO₂ is almost irreversible chemically absorbed. Hollingsworth et al. used a hydrated (0.7 mol L⁻¹ H₂O) 0.1 mol L⁻¹ trihexyltetradecylphosphonium 1,2,4-triazolide, [P66614] [124Triz] solution in acetonitrile to reduce CO₂ at Ag, Au and Pt electrodes. This ionic liquid has been shown to chemisorb CO₂ through equimolar binding of the carbon dioxide with the 1,2,4-triazolide anion [16,17], favouring formate formation by a low energy route (-0.7 V vs. Ag/AgNO₃ with 95% Faradaic efficiency in formate on Ag electrodes). Thus, literature shows that the main products from CO₂ reduction in IL-based electrolytes are CO and formate. To our best knowledge there are only three works that report syngas production, the work of Zhao et al. [6] the work of Asadi et al. [18] in which the control of the H₂/CO ratio is achieved by the tuning of applied potential and the work of Liu et al. [19] in which the control of the H₂/CO ratio is achieved by manipulation of the pH on either side of an anion exchange membrane, as well as the use of bimetallic Ag/Ni catalysts on the cathode. In the former work, supercritical CO₂ and water were electrolyzed at a copper cathode in the hydrophobic ionic liquid, 1-*N*-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), using a platinum anode. The electrolysis products detected were CO, H₂, and traces

of formic acid. However, large overpotentials were required for carrying out electrochemical reduction.

In the majority of systems using ionic liquid-based electrolytes, H₂ production is suppressed due to the cation forming a monolayer on the electrode surface [20] and CO is mainly produced, the tunability of H₂/CO is very limited, or the selectivity for syngas is poor. In conventional aqueous-based electrolytes hydrogen evolution is a strong competing reaction and generally electrocatalytic systems are not selective for syngas, or produce mainly CO (H₂/CO ratios near zero) [21]. Thus, flexible processes that can produce syngas with a tunable H₂/CO ratio are needed.

Pressure is a process parameter influencing significantly many chemical systems. As implementing systems that work above atmospheric pressure is not as straightforward as operation at atmospheric pressure, this parameter is often not studied. A limited number of studies employing high-pressure for the electrosynthesis of valuable compounds using CO₂ as a reactant that involve the use of ILs have been reported [11], namely, Hiejima et al. [22] studied the electrosynthesis of 2-phenylpropionic acid from CO₂ and found out that current efficiency that was low under ambient conditions, drastically increased with temperature and pressure, which was mainly explained by the increase of the diffusion coefficient of the reactant in the IL.

Current density and selectivity of the CO₂-water co-electrolysis was also found to be dependent on pressure [21]. To our best knowledge, there is only one study that was carried out at high-pressure using an ionic liquid based-electrolyte [6]. In fact, high-pressure CO₂ reduction stands out as being one of the most promising methods for achieving a commercial electrochemical process, as it was demonstrated that current densities of 3 A cm⁻² could be obtained, using an aqueous phosphate buffer electrolyte [23]. Current densities of this order of magnitude were only recently reported for high temperature (~800–900 °C) solid oxide electrolyzers [24,25].

To design a commercial semi-continuous or continuous high-pressure process for CO₂ electrochemical reduction is a challenging task. Reactants must be fed through gas-tight fittings rated for high pressure and products removed also through gas-tight fittings. Electric insulation of the electrochemical reactor must be accomplished. The pressure of the system must be controlled, so that a pressure difference between the cathodic and anodic compartment of the flow cell doesn't arise, which would cause the burst of the separator. Alternatively, an ionic conducting material with a suitable pressure rating would have to be used, or developed for the separator. This work reports a first development phase in which a single compartment high-pressure electrochemical cell was used and the experiments were carried out in batch mode, under CO₂ static pressure. The use of a single compartment high-pressure electrochemical cell presents also its difficulties. The use of a noble metal anode, such as Pt, may cause the oxidation of the products produced at the cathode, or can be poisoned [12] by the CO arising from CO₂ reduction. The use of a sacrificial anode may contaminate the electrolyte producing the correspondent cations that can be subsequently electrodeposited at the cathode.

Katoh et al. studied the electrochemical reduction of CO₂ by bimetallic Zn-Cu cathodes in aqueous 0.05 M KHCO₃ electrolytes at atmospheric pressure and 2 °C [26]. These researchers observed partial current densities for CO of less than 1 mA/cm². The use of bimetallic Zn-Cu cathodes coupled with ionic liquid-based electrolytes has not yet been reported. This work reports results of the development of electro-catalysts made-up of abundant common metals (Cu and Zn) and of a process for the production of syngas from CO₂ with a controlled H₂/CO ratio by tuning the catalyst composition by electrochemical reduction at near room temperature and at high-pressure using an ionic liquid with a controlled concentration of water as electrolyte. A zinc sacrificial

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