Ag-Co bimetallic catalyst for electrochemical reduction of CO2 to value added products

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A B S T R A C T

Direct electrochemical reduction of carbon dioxide to values added products is one of the most promising and challenging techniques. Moreover, the lack of availability of efficient, selective and stable electrocatalysts is a major difficulty for efficient CO_2 reduction. Various materials including metals, metal oxides, and metal complexes have been studied to increase the Faradaic efficiency, selectivity, and to reduce the energy input for the generation of hydrocarbons. Herein, we report a non-noble bimetallic electrocatalysts based on Ag-Co that is hardly evaluated for the electrochemical reduction of CO_2 in-spite of the proven synergetic effect of bimetals for various chemical reactions. Therefore, the present study investigates the role of bimetallic electrocatalyst for the CO_2 electrochemical reduction. A bimetal electrocatalyst is synthesized by Co and Ag metals to investigate the effect of the bimetal over gas phase CO_2 electrochemical reduction. It is found that though the chosen metals are individually selective for the CO formation but the combination results in CH_4 and C_2H_4 formation along with CO. The maximum Faradaic efficiency found for CH_4 is 19.5% at 2 V using Ag-Co.

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1. Introduction

The growth in human population and rapid industrialization for the advancement of society caused rapid energy consumption and is estimated to be more than double by 2050 [1]. So far major portion of the energy consumption and demand is covered by fossil fuels, which are expected to remain the leading energy source to fulfill the increased energy demand for the near future. However, the extraction of energy from the limited fossil fuels in the form of value added chemicals and transportation fuels led to increased emission of carbon dioxide (CO_2) and other toxic gases (e.g., NOx, SOx, etc.), which has led to many global problems such as climate change, global warming, ocean acidification etc. [2,3]. Moreover, it was predicted that in coming four to five decades, an about 496 gigatonnes of CO_2 will be produced due to combustion of fossil fuel by existing infrastructure and industrialization [4]. Hence in order to limit the aforementioned environmental issues, the United Nations Intergovernmental Panel on Climate Change (IPCC) has intended to reduce a 50–85% of the global CO_2 emission by 2050 (compared to 2000 levels) [5]. However, reducing CO_2 emission up

to this level is a major challenge for the scientific community. The effective ways to accomplish this challenge is to replace fossil fuels with carbon-neutral alternative renewable energy sources e.g., solar and wind power. However, the intermittent nature of these renewable energy sources produced irregular electrical power, which limits their integration into the grid [6]. Hence, a viable technology to store the renewable energy in more appropriate fashion is necessary. Electrochemical reduction of carbon dioxide (ERC) driven by these renewable energy sources would be one of the effective technologies to store the renewable energy in chemical bonds, in the form of high density fuels and chemicals [7,8]. Direct ERC is a promising method as it can be driven by renewable energy sources, proceeds at moderate temperature and atmospheric pressure, its capability to generate high energy density product can be tuned by varying reaction conditions [9,10]. In direct ERC, the humidified gaseous CO_2 and water are fed at cathode and anode of the electrochemical reactor. The water oxidizes and produce O_2, H^+ and electron. The H^+ migrates from anode to cathode through a cationic membrane and electron travel through the outer circuit. At the cathode the CO_2 reduces by reacting with the electrons and H^+. Various products forms at cathode depending upon the number of electrons able to react with the CO_2 and H_2 also forms as a by-product. Hori et al. reported that the CO_2 reduction reaction yields CO, HCOOH, CH_4, alcohols,

and other hydrocarbon products, in which the selectivity is highly dependent on the adsorption properties of reactants on electrode metals [11]. Amongst various products, CO is one of the desirable products, as it may serve as an important raw material in the chemical process industry to produce various chemicals as well as synthetic fuels. Despite paving a path towards renewable energy storage, the hydrocarbons produced from ERC may also contribute to mitigate CO_2 emissions. However, development of efficient and selective electrocatalysts is one of the key barriers identified by the Department of Energy (DOE) [12].

So far, various electrocatalysts such as Au, Cu, Ru, and Mo etc., have been studied to electrochemically reduce CO_2 to CO, hydrocarbons, and alcohols with a high selectivity [13]. However, the metal electrocatalysts suffer a major setback due to the large overpotential and poisoning [14]. Besides metals, transition metal complexes such as phthalocyanins [15], porphyrins [16], bipyridines [17] were also tried for ERC to value added products. However, the transition metal complexes could address the problem of high overpotential upto some extent but formation of fuel kind of products remains a challenge [18]. It has been noticed that almost all the studies in the field of CO_2 electroreduction are primarily focused on either pure metal or metal complex electrocatalysts [19,20]. Therefore, to tackle the issues; search for new alternatives is going on. Furthermore, it is important to focus on less utilization of noble metals in the design of electrocatalysts and finding a facile synthesis process for the efficient and selective reduction of CO_2 to value added products. Alloying (or bimetallic compounds) is one of the most impactful candidate approaches to reduce the material cost. Bimetallic compounds are used to tune the strength of the intermediate of ERC to achieve high selectivity [21]. Alloying is also done with metals having high overpotential for hydrogen evolution reaction (HER) to suppress the competitive HER over direct ERC. Furthermore, metals which are inactive towards ERC can be made active with addition of foreign metals. As different metals have different affinity for the adsorption of oxygen and carbon, which in-turns make selective and stable intermediates on the catalyst thus enhance the selectivity of the electrocatalysts. In this regards certain combinations of the metals have been tried such as Au-Cu, Cu-In, Cu-Sn, Pd-Pt, Pd-Cu etc., which primarily have noble metals [22–27]. Initial oxidation pre-treatment of Cu electrode to generate high surface area with grain boundaries was found to be necessary for high selectivity of the CO. Further on comparing the effect of Zn and Sn as second metal in Cu alloy showed that metals with high overpotential for HER inhibits H_2 evolution without affecting the CO_2 electroreduction by the primary metal. DFT studies suggests that Indium deposited on the edge sites decreases the H_2 evolution, whereas, ERC occurs at more active corner sites. Azuma et al. reports relationships between metal catalysts and corresponding products [28], CO and hydrocarbons are the primary products over d-metals. Thus, alloying silver with inexpensive cobalt should be a promising strategy for the selective reduction of aqueous CO_2 to CO and other value added products. Recently, a few studies suggested that adjustment of binding energies of the intermediate with the catalyst may promote the formation of a particular product [22,29]. It has been found that d-band of the transition metals plays a crucial role in determining the binding strength by interacting with the adsorbate [30]. The basic reason for the change in binding strength is the charge (electron) transfer in these bimetallic systems [29]. These preliminary studies have opened up an avenue to investigate the effect of bimetallic electrocatalysts for the ERC to synthesize fuel kind of products. It has been observed that most of the earlier studies were based on Cu as one of the metal in bimetallic system [22,29,30].

In the present study, Co and Ag are chosen to investigate the effect of their combination for the dERC. The rationale to choose Co is that it is a transition metal having incompletely filled d-orbital. Also, the selectivity to higher hydrocarbons of Co catalyst relative to methane increases with increasing CO_2:H_2 ratio. On the other hand, Ag possesses only one electron in its outermost shell along with empty p- and d-orbitals. Therefore, these two metals have been chosen with the hypothesis that the combination of Ag and Co might trigger a change in the binding energy of the bimetal with CO_2 due to the electron transfer. This change in binding energy may lead to modified physical and chemical properties of the bimetal-CO_2 system and in-turn influence the CO_2 reduction reaction. Therefore, Ag-Co electrocatalyst was synthesized and thoroughly characterized to understand the role of bimetals for the gaseous CO_2 electroreduction. Half-cell and full cell reactions were carried out using bimetallic electrocatalyst to identify and quantify the reaction products.

2. Experimental section

2.1. Materials

Nitrate compounds of Co and Ag were used as the metal precursors. $Co(NO_3)_2$ was purchased from Qualigens and $AgNO_3$ were procured from Merck. Sodium borohydride, was purchased from Loba Chemie. Potassium bicarbonate ($KHCO_3$), was also procured from Loba Chemie. Pt/C (40 wt% Pt) was purchased from ElectroChem, Inc. USA. All the chemicals were used without further purification and de-ionized water was used in all the experiments unless stated otherwise. Gas diffusion layer from CeTech was used as backing layer for electrode preparation. Nafion membrane (Nafion-117) and Nafion dispersion (5 wt%) were procured from DuPont, USA.

2.2. Synthesis of the bimetallic Ag-Co electrocatalyst

The bimetallic Ag-Co electrocatalyst was prepared by simultaneous reduction of $Co(NO_3)_2$ and $AgNO_3$, using sodium borohydride ($NaBH_4$) the reducing agent. Aqueous solution (0.1 M) of metal precursors was reduced by dropwise addition of excess amount of $NaBH_4$ (0.1 M). The reaction was carried out in ice bath to avoid secondary reactions of $NaBH_4$. The reaction mixture was agitated continuously during the reaction. The resulting precipitate was filtered, washed and dried at 60 °C to get the Ag-Co electrocatalyst [31].

2.3. Preparation of electrodes and membrane electrode assembly (MEA)

Catalyst ink for cathode (or working electrode) was prepared by dispersing the bimetallic electrocatalyst in appropriate solvent along with Nafion dispersion. The electrocatalyst ink was then coated over the gas diffusion layer followed by drying. The Pt/C and the Nafion dispersion as binder were used to prepare the anode electrocatalyst ink. This ink was coated over the gas diffusion layer using spraying technique and dried to get the anode. The electrocatalyst loading for anode and cathode was kept at 0.5 mg cm^{-2} and 2 mg cm^{-2}, respectively. The area of the electrodes was about 9 cm^2. The Nafion membrane was treated as per the standard procedure [32] before the experiments. The membrane electrode assembly was prepared by sandwiching the Nafion membrane in between anode and cathode at specific temperature and pressure [33].