



Sustainable Production of Fuel from Electrochemical Reduction of Carbon Dioxide

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Abstract:

Carbon dioxide being a very stable molecule, has always sought the attention of researchers globally, and its efficient fixation is still a challenging task. Electrochemical reduction of CO₂, is one of the methods to fix this molecule, which can result in products like methanol, formic acid, methane etc. that can be efficiently used as alternative energy carriers. However, CO₂ electroreduction is not a very feasible reaction without the use of catalysts because of the high overpotential, slow reaction kinetics, and other competing reactions. Hence, use of the efficient catalyst is of key importance in this reaction, as it also determines the selectivity of products. In this present work, an electrochemical reactor is developed and fabricated for the electrochemical conversion of CO₂ into fuel. Catalysts, CuO and ZnO are synthesized and characterized for electrochemical reduction of CO₂ into methanol. The absorbed CO₂ in potassium bicarbonate solution is fed into the electrochemical reactor. It is found that the catalysts are active towards CO₂ electroreduction and highly selective for methanol production. The yield of the methanol for CuO and ZnO are found to be 8.7% and 5.4% at 2.0 V and 2.5 V, respectively.

Keywords: Carbon Dioxide; Copper Oxide; Electrochemical Reduction; Methanol; Zinc Oxide

Introduction

The worldwide increase in energy demand and environmental problems especially global warming has put an enormous pressure on the researchers to explore some alternative, which should not only be sustainable but also tackle the environmental issues. CO₂ is considered as one of the major contributors of global warming. It has been found that using electrochemical reduction technique, it is possible to convert CO₂ from the environment and at the same time, the formed reaction products may be used as fuel (like methanol, methane etc.) [1,2]. However, there are challenges for low yield of the reaction products and high overpotential with the conventional electroreduction procedure [3]. Electrocatalyst plays an important role for the CO₂ reduction and selective formation of the reaction product. In this paper, an advanced continuous electrochemical reactor is developed for the electrochemical reduction of CO₂ (ERC). Two different catalysts are synthesized and used for the selective formation of methanol using ERC.

Experimental

Cu(NO₃)₂·3H₂O (Merck, India) was taken as precursor and precipitated with appropriate amount of ammonia solution. The resulting mixture was aged for 5-6 hours and then the precipitate was filtered and washed with water. The precipitate was dried and calcined at 360°C for 24 hours in order to get CuO electrocatalyst. ZnO was also synthesized in a similar manner.

The crystal structures of the prepared catalysts were identified by Rigaku high power XRD with CuK α radiation ($\lambda = 0.154$ nm) at 55 kV in the 2θ range of 10-90°. The prepared catalysts were further characterized by N₂ adsorption-desorption at 77K. The specific surface area of the catalysts was determined by Brunauer-Emmett-Teller (BET) method in the Beckman Coulter surface area analyzer (SA 3100).

The electrode activity towards CO₂ reduction was evaluated using cyclic voltammetry (CV). The CV was recorded in 0.5 M KHCO₃ saturated with CO₂ using Pt wire as counter electrode and Ag/AgCl sat. KCl as reference electrode, at the scan rate of 0.01 V.s⁻¹. The working electrode was the CuO or ZnO electrode with 2 mg.cm⁻² catalyst loading.

The ERC was done in an electrochemical reactor having anode, solid polymer electrolyte, and cathode assembly with continuous supply of CO₂ saturated KHCO₃ solution for the reaction. The electrolyte used was cation exchange membrane

(nafion-117). Cathode was made up of gas diffusion layer and 2 mg.cm^{-2} of catalyst loading (CuO or ZnO) on to it. However, anode was made up of gas diffusion layer electroplated with Cu_2O for all the experiments. Chronoamperometric tests were performed in the reactor using potentiostat/galvanostat (CHI6008B). At the cathode, CO_2 saturated 0.5M KHCO_3 solution was fed at a flow rate of 1.5 mL.min^{-1} . At the anode side, water was passed at the flow rate of 2 mL.min^{-1} . The reaction products were analyzed by gas chromatograph (Varian CP 3800), equipped with FID detector and a suitable column.

Results And Discussion

The XRD pattern of the synthesized catalysts is shown in fig.1. It can be seen that CuO and ZnO possess single phase monoclinic structure and wurtzite structure, respectively. The crystallite size was calculated using Scherrer formula and found to be 52.5 nm for CuO and 49.5 nm for ZnO.

The BET surface area of CuO and ZnO was found to be $9.9 \text{ m}^2.\text{g}^{-1}$ and $15.9 \text{ m}^2.\text{g}^{-1}$, respectively. The corresponding Barret-Joyner-Halenda (BJH) calculation, which is based on desorption data depicts that pore size distribution ranges from 4 to 40 nm for CuO and 10 to 50 nm for ZnO.

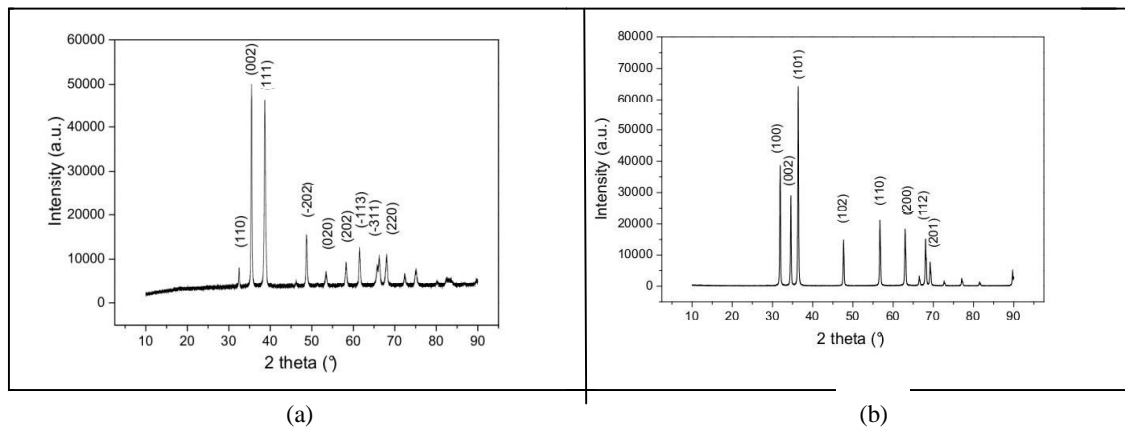


Figure 1: XRD pattern of the synthesized catalysts (a) CuO, (b) ZnO

Cyclic voltammograms for the CuO and ZnO are shown in fig. 2. It can be seen in the fig. 2 that in the presence of CO_2 , the onset potential (the potential at which 0.1

mA.cm⁻² current density is observed) of the cathodic current was -0.85 V (vs. SHE) using CuO and -1 V (vs. SHE) using ZnO.

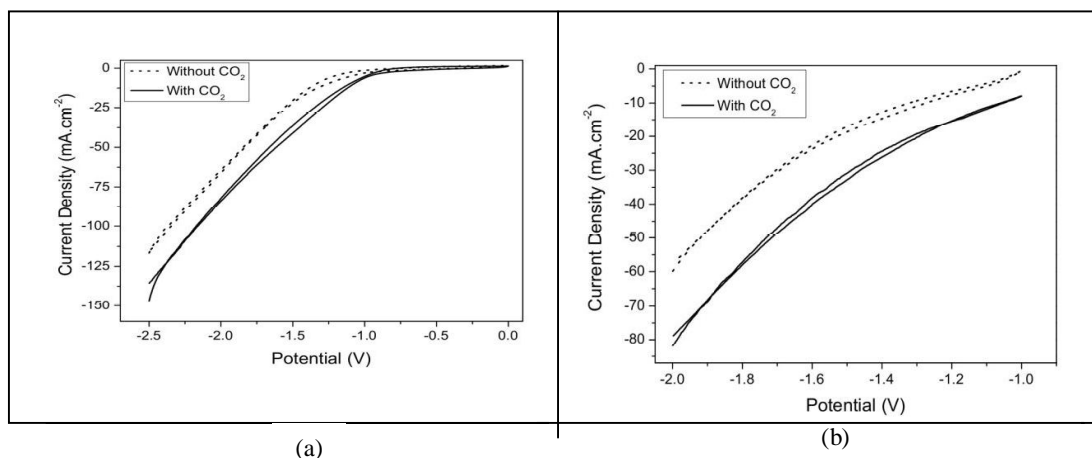


Figure 2: Cyclic voltammograms for (a) CuO, (b) ZnO

In chronoamperometric measurements different cell voltages were applied to find the optimum value for efficient ERC. The GC analysis of the reaction products showed that only methanol was formed selectively using both the catalysts. It can be seen in fig. 3 that the optimum value for efficient ERC to methanol is about 2 V for CuO and 2.5 V for ZnO. It clearly substantiates the onset potentials obtained in CV analysis. The maximum methanol yield is about 8.7% for CuO and about 5.4% for ZnO catalyst.

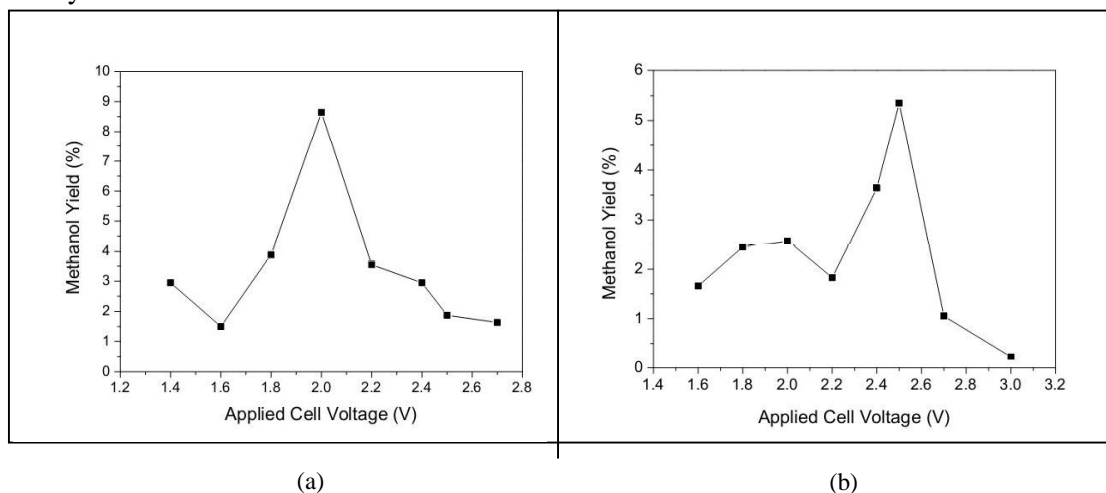


Figure 3: Methanol yield using (a) CuO, (b) ZnO as catalyst

Conclusion

The CuO and ZnO catalysts were successfully synthesized by the precipitation method for the electrochemical reduction of CO₂. The BET surface area of ZnO was found higher (15.9 m².g⁻¹) as compared to CuO (9.9 m².g⁻¹). However, the methanol yield for CuO was 38% higher than ZnO. These results are very encouraging and the study is required to be done in a great extent considering the challenges of the ERC technology.

Reference

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