Reactor Engineering for the Photoelectrochemical Performance Optimization in CO_2 Reduction to Methanol and Isopropanol

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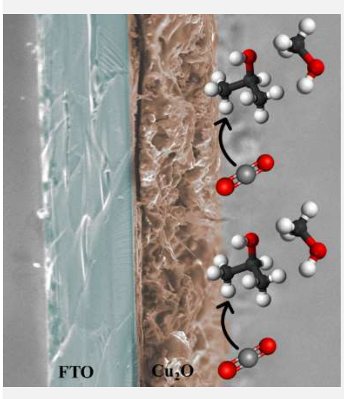

Herein, we demonstrate how reactor engineering can enhance the photoelectrochemical performance of CO_2 reduction to methanol and isopropanol, using commercial Cu_2O as a model catalyst. Operational conditions play a crucial role in controlling gas solubility and, consequently, photoelectroactivity and product distribution. The evaluated parameters were electrolyte type, applied potential, reaction temperature, purging process (batch or continuous), and the use of Venturi tube. KOH was found to be a more efficient supported electrolyte because it increased the local pH, favoring the formation of C_n compounds. Additionally, lower temperatures are detrimental to the reaction rate, while higher applied potentials must be avoided to prevent the accumulation of charges over the photoelectrode surface. Both continuous process for CO_2 purging, and the use of a Venturi tube, improved the isopropanol selectivity by increasing the gas concentration in the aqueous solution.

Introduction

Carbon dioxide reduction reaction (CO2RR) has been investigated and upgraded over the years since the CO2RR can be performed under mild and controllable operational conditions through photoelectrochemical (PEC) reactions [1]. Photoactive materials minimize the thermodynamic barrier imposed by CO_2 stability and reduce the external energy input [2]. Several reports regard the catalytic activity of materials and correlate the overpotential and selectivity to materials' features [3-5]. However, few emphasize the role of operational conditions and reactor design in the system's overall efficiency.

Thus, we provide a systematic experimental study of CO2RR driven by a homemade PEC filter-press reactor, using commercial Cu-based photoelectrodes as a model photoelectrocatalyst. We also detail the onset potentialities for the formation of liquid products, making a correlation between the PEC performance and the operational conditions, such as applied potential, reaction temperature, process for purging CO_2 (batch/continuous), type of electrolyte, and the use of Venturi tube.

Material and Methods

Fig. 1 depicts the homemade filter-press photoelectrochemical reactor used for the CO2RR. A 100 W halogen lamp having ~100 mW cm^{-2} of incident light illuminated the working electrode through a quartz window. The cathode and anode chambers are separated by a cation exchange membrane, Nafion 117. A stainless steel 304 was used as the counter-electrode, while 5 cm^2 Cu_2O/FTO was employed as the working electrode, as showed in Graphical Illustration. Cu_2O was purchased from Sigma-Aldrich and was deposited over FTO by spray coating. An Ag/AgCl 3.0 M KCl was used as reference electrode. The catholyte was purged with a constant flow of N_2 for 20 min, followed by saturation with CO_2 gas for the same time. Reactions at different applied potentials were carried out for 60 min. The experiments were performed in a discontinuous mode, and the recirculation of 0.5 M electrolyte was kept at a 14 mL min^{-1} flow rate. Liquid samples were analyzed by ^1H NMR.

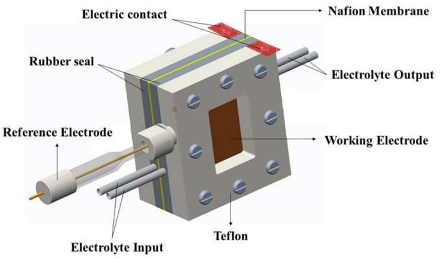

Figure 1. PEC reactor for CO2RR.

Results and Discussion

One of the main drawbacks for CO2RR is the low solubility of CO_2 in aqueous media (33 mM at 1 atm and 25 °C) [6]. Different approaches can be used in the effort to overcome this issue and some easy-applicable strategies are the use of (i) basic electrolytes; (ii) lower reaction temperatures; and (iii) systems to improve the gas solubility. Considering that basic electrolytes react with CO_2 to form carbonate species as CO_3^{2-} and HCO_3^- [7], our first attempt was to evaluate the influence of three different supported electrolytes, Fig. 2. The influence of the electrolyte and applied potential in the product distribution are evident. KOH led to superior PEC performance and better selectivity to isopropanol. On the other hand, as the applied potential increases, charges will accumulate near the photoelectrode surface, blocking the active sites for CO_2 adsorption and decreasing its local concentration. Consequently, the highest bias of 1.2 V *vs.* Ag/AgCl often is detrimental to the C_n formation, probably due to the lack of local CO_2 for the reduction reaction [8, 9].

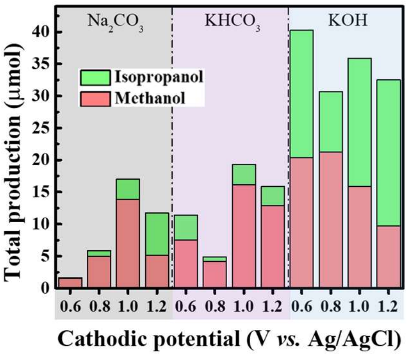

Figure 2. PEC CO2RR using different electrolytes and applied potentials at 25 ºC.

Fixing the supported electrolyte and the cathodic potential, the other operational conditions can be investigated, Fig. 3. Firstly, the CO_2 purging was evaluated in a continuous process at 25 ºC – instead of the previous batch process – and the total production increased three times, indicating one limiting factor for the formation of methanol and isopropanol is the CO_2 availability in the reaction medium. The temperature is also a critical operational parameter since, even when using the continuous process for CO_2 purging, lower temperatures result in poorer PEC performance. The Arrhenius law states that the rate of chemical reactions is directly dependent on the temperature; thus although the gas solubility being increased at lower temperatures, the CO2RR reaction rate is negatively impacted.

The Venturi tube also improves the gas-liquid contact and enhance the CO_2 solubility in the aqueous solution at 25 ºC during the purging process. The obtained result was remarkably successful, demonstrating once more the importance of enhancing the CO_2 solubility to improve the quantity of molecules available for the reaction and facilitate the generation of C2+ chemicals.

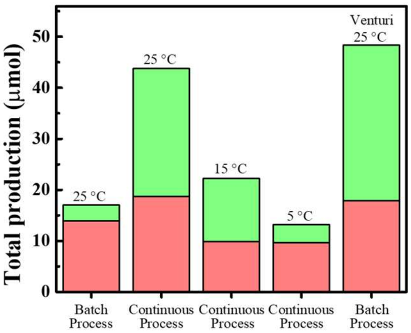

Figure 3. PEC CO2RR using different reaction temperature and Venturi tube in 0.5 M Na_2CO_3 and applying -1.0 V *vs.* Ag/AgCl.

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Conclusions

We proved that reactor engineering could enhance the energy efficiency of the CO2RR. The PEC reactor generated methanol and isopropanol and their distribution depend on operational conditions, such as supported electrolyte, applied potential, temperature, operation mode of the CO_2 bubbling, and the use of a Venturi tube.

Acknowledgments

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