Concomitant advanced oxidation process with CO_2 electro-reduction with reticulated electrodes

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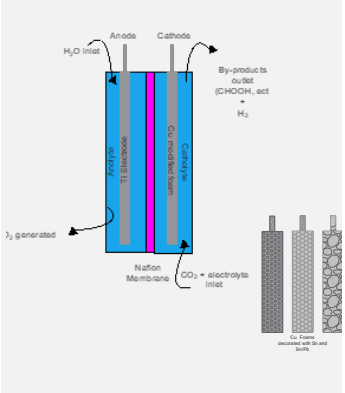

This work aimed to conduct the CO_2 electro-reduction in an H-type cell with Cu foam electrodes, assessing the effect of two main variables on methanol, formic and acetic acid concentration: decorating material (Sn, Ag, Pb, Sn/Ag and Sn/Pb) and electrolyte support (bicarbonate and wastewater from confectionery industry).

It was found that methanol was the main product with the electrodes decorated with Ag. The samples were measured in HPLC and GC; reaching methanol concentrations between 4 mM and 9mM. The methanol production was enhanced when conducting the CO_2 electro-reduction with wastewater from confectionery industry in the anodic compartment instead of bicarbonate solution.

Introduction

During the latest century the levels of CO_2 in the air have increased considerably, as the main by-product of the combustion of fossil fuels, due to this, high concentrations are provoking an environmental damage, that is generating several natural hazards, such as dryness, floods, among others [1].

Nowadays, electrochemical technology able to reduce CO_2 in air is being developed. These new methods not only can decrease the levels of CO_2, but also can reduce it and generate added-value products, that are able to be used in a wide variety of industries. The efficiency depends on the traits of the electrocatalyst and products such as methanol, formate, acetic acid, oxalic acid [2], acetone, and more are produced.

This work aims to present the results when conducting the CO_2 electroreduction in a H-type cell with Cu reticulated electrodes. Two variables were assessed, decorating material Sn, Ag, Pb, Sn/Ag and Sn/Pb and the electrolyte support 0.1 M $KHCO_3$ and wastewater from confectionery industry.

Material and Methods

The CO_2 electro-reduction was carried out by modifying copper foams with Sn, Ag, Pb, Sn/Ag and Sn/Pb by electroplating. Subsequently, the foams were characterized by cyclic voltammetry, chronoamperometry and focal microscopy.

For CO_2 reduction, an H-type cell was employed, using a Nafion 117 membrane to separate the anodic and cathodic chamber. In the cathodic compartment, modified foams Sn, Ag, Pb, Sn/Ag and Sn/Pb were used as working electrodes, Ag/AgCl as reference electrode, while in the anodic compartment a titanium mesh counter electrode was used. Bubbling nitrogen in the aqueous system before each treatment. For the first set of experiments, $KHCO_3$ was used as electrolyte in both chambers at a concentration of 0.1 M, for 20 minutes.

In a second set of experiments, wastewater from confectionery industry and $KHCO_3$ was used as electrolyte in cationic chamber at a concentration of 0.1 M, for 60 minutes. The last experiment was used as electrolyte wastewater from confectionery industry, in both chambers for 60 minutes.

The samples were analysed by high performance liquid chromatography (HPLC) to identify and quantify organic acids and gas chromatography (GC) to quantify methanol.

Results and Discussion

Figure 1 shows the temporal concentration profiles of acetic acid and formic acid when using copper electrodes decorated with silver. It worth noticing that due to the available space the results with the other electrodes are not shown. However, the best results in terms of methanol concentration (9 mM) were obtained with the Cu/Ag electrode and therefore the results in terms of organic acids concentration with this electrode were elected to be shown in figure 1. Such results were obtained using the bicarbonate solution as support electrolyte in the cathodic chamber and wastewater in the anodic compartment.

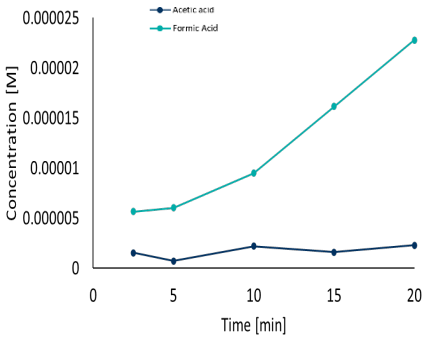

Figure 1. Temporal concentration profiles of carboxylic acids using copper foam electrode decorated with Ag, -1V current, Ag/AgCl reference electrode and Pt counter electrode. Support electrolyte 0.1 M $KHCO_3$.

Table 1 summarizes the effect of the support electrolyte on the organic molecules concentration when the Cu/Ag foam electrode is used. It can be observed that the methanol production is favoured when the wastewater is used in the anodic chamber instead of the bicarbonate solution.

Thus, it can be observed that Ag modified electrodes offer a huge advantage in methanol production, due to the ability to generate a mix of C_1 products. Another advantage is that high pressures are not required and electrolytes can improve the generation of by-products[3].

Table 1. Effect of electrolyte on concentration of methanol, formic acid and acetic acid after 60 minutes of reaction conducted with Cu/Ag foam electrode

Electrolyte	Methanol (M)	Formic acid (M)	Acetic Acid (M)
0.1 M $KHCO_3$/0.1 M $KHCO_3$	$4x10^{-3}$	$1.5x10^{-5}$	$3x10^{-5}$
0.1 M $KHCO_3$/wastewater	$9x10^{-3}$	$1x10^{-5}$	0
Wastewater/wastewater	$4.8x10^{-4}$	0	$2x10^{-4}$

Conclusions

The electrocatalysts using the foams offer advantages due to the morphology and geometry, in addition to using copper as support and the various transition metals with which they are modified, provide characteristics that favor the generation of various value-added by-products. Among the assessed electrodes, methanol production was favored by the use of Ag/Cu electrode and the use of bicabonate solution in the catode compartment and wastewater from a confectionery industry in the anodic compartment. These results are relevant in the context of circular economy since the present process uses residues from other processes as raw materials.

Acknowledgments

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