Communication

Direct Electrochemical Reduction of Bicarbonate to Formate Using Tin Catalyst

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Table S1. List of abbreviations

Abbreviation	Full name
^{1}H NMR	Proton nuclear magnetic resonance
DMSO	Dimethylsulfoxide
D_2O	Deuterated water
LSV	Linear Sweep Voltammetry

Figure S1. 3D rendered design of Teflon H-cell used for the experiments.

The cell consists of two compartments (Anodic (1) and Cathodic (2)) filled with bicarbonate solution and separated by a proton exchange membrane (Nafion membrane) to prevent re-oxidation of reduced products on the cathode. The anodic compartment contains the counter electrode (3) (platinum foil), where water splitting takes place. In the cathodic compartment there is the working electrode (5) (Sn foil) where the CO_2 is reduced and the reference electrode (4) (Ag/AgCl (0.21V) is used to maintain a stable potential reading. For the saturation of solution with CO_2 outlets (6) and inlet (7) for gas were used.

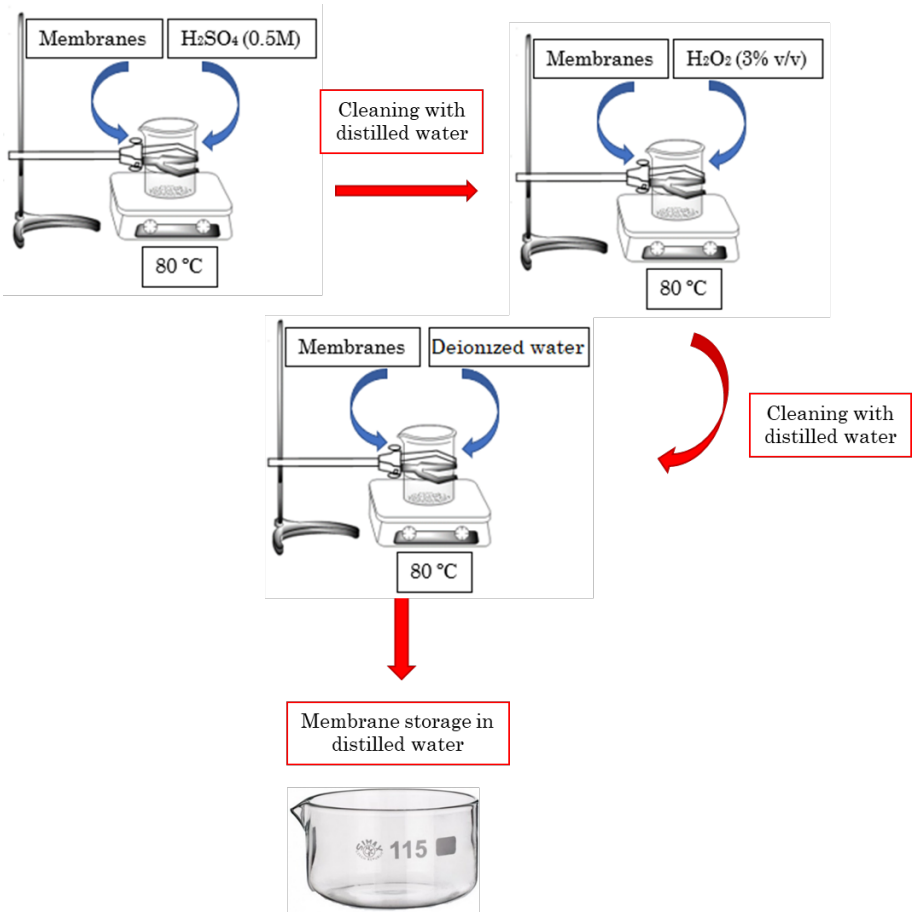

Figure S2. Nafion membrane cleaning procedure:

1.-Cut the membranes (using scissors) into pieces with desired size, but small enough to fit into the bottom of a 1l beaker.
2.-Immerge the membranes into 1l beaker with H_2SO_4 preheated up to 80 degrees with bath oil and leave them during 1h with stirring.
3.-Clean the membranes with distilled water immerging and shaking them into a big crystallizer before continuing with next step.
4.- Immerge the membranes into 1l beaker with H_2O_2 preheated up to 80 degrees with bath oil and leave them during 1h with stirring.
5.-Clean the membranes with distilled water immerging and shaking them into a big crystallizer before continuing with next step.
6.- Immerge the membranes into 1l beaker with distilled water preheated up to 80 degrees with bath oil and leave them during 1h with stirring.
7.-Store the membranes into a big crystallizer with distilled water (the membranes must be wet) and cover it with watch glass.

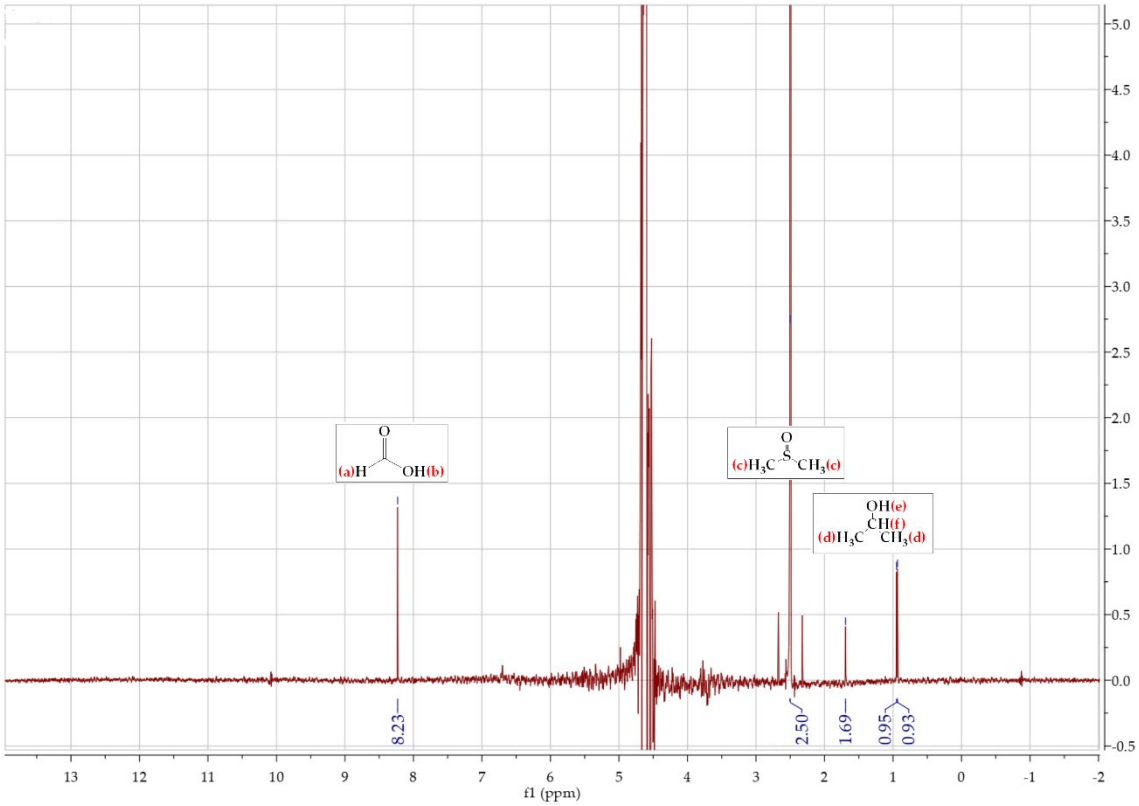

Figure S3. ^{1}H NMR spectra of products after electroreduction.

In order to reduce the intensity of water peak to make other peaks more visible a pre-saturation around 4.5ppm was applied. The peak of proton (a) appears around 8.23 ppm and corresponds to the carbonylic proton of formic acid/formate. Proton (b) should be observable around 11ppm, but the slightly acidic media makes it be dissociated and not visible in NMR. Proton (c) corresponds to the DMSO protons used as internal reference for quantification and it is observable at 2.5 ppm with its two rotational peaks. Proton (d) and (e) are observable at (0.95-0.92 ppm) and 1.69 ppm respectively corresponding to isopropanol residues used to clean the reactor. Finally, proton (f) is not observable because its merged with the attenuated water peak.