Electrochemical conversion of CO_2 to formic acid in a microfluidic device

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INTRODUCTION

Since the industrial revolution, energy demand has gradually increased due to economic growth, thus causing high CO_2 emissions [1]. For this reason, many companies and research centers employ resources to develop appropriate processes for the conversion of CO_2 into chemicals and/or fuels. A promising strategy to valorise waste-CO_2 is its cathodic reduction (CO_2CR) into various chemicals, including formic acid (FA). The use of microfluidic cells allows to work with lower cell potentials than conventional cells and, also, to obtain significant FA concentrations even in the absence of supporting electrolyte [2]. Hence in this context, the present work focused on the effect of supporting electrolyte concentration (SE), flow rate (Q), current density (j) for CO_2CR.

RESULTS AND DISCUSSION

Effect of the concentration of supporting electrolyte

Some authors have previously shown that CO_2CR to FA depends significantly on the nature of SE and on the pH value. As shown in Fig. 1a, in the conventional reactor, the concentration of Na_2SO_4 strongly affected both the final concentration of FA and the cell potential (ΔV). Also in the microcell, as shown in Fig. 1b, a remarkable effect of the concentration of Na_2SO_4 on the production of FA was observed. In fact, the lower the concentration of Na_2SO_4, the higher the production of FA. However, a very small effect on ΔV was observed [2].

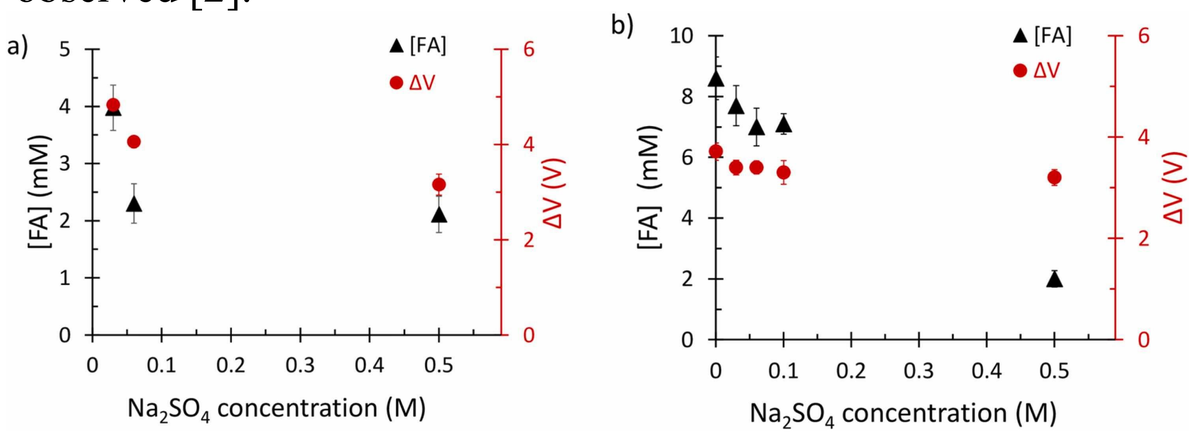

Figure 1. Effect of the concentration of SE on the conversion of CO_2 to FA and on the ΔV in a conventional laboratory macro cell under batch conditions (Fig. 1a) and in a microfluidic cell equipped with a h of 75 μm (Fig. 1b).

Results without the supporting electrolyte

To reduce process costs and to work in the complete absence of electrolyte, a series of electrolysis was carried out using only water saturated with CO_2. These electrolysis focused on the effect of the different distances between the electrodes (75, 120 and 250 μm) and j (– 4, – 8, – 12 and – 16 mA cm^{-2}) [2].

Entry	h (μm)	j (mA cm^{-2})	[FA] (mM)	ΔV (V)
1	75	8	5.0 ± 0.48	3.5 ± 0.15
2	120	8	7.0 ± 0.40	3.7 ± 0.20
3	250	8	5.5 ± 0.25	5.0 ± 0.20

Table 1. Electrolyses carried out without SE with Q at 0.4 mL min^{-1} and of j at – 8 mA cm^{-2}.

Effect of current density and flow rate

The effect of two parameters such as j and Q in the micro-reactor cell was investigated. As shown in Fig. 3a, the plot [FA] vs. j resulted in a curve with a maximum for a j of – 8 mA cm^{-2}. Moreover, the increase of j resulted in higher ΔV (Fig. 2a) and, therefore, in higher energy consumption.

Concerning the effect of Q, it was observed that a lower Q resulted in a higher production of FA (Fig. 2b) because of the higher residence time (τ). Instead, when Q was increased, a lower τ was achieved, thus resulting in lower final concentrations of FA, in lower conversions of CO_2 but in higher Faradic efficiency [2].

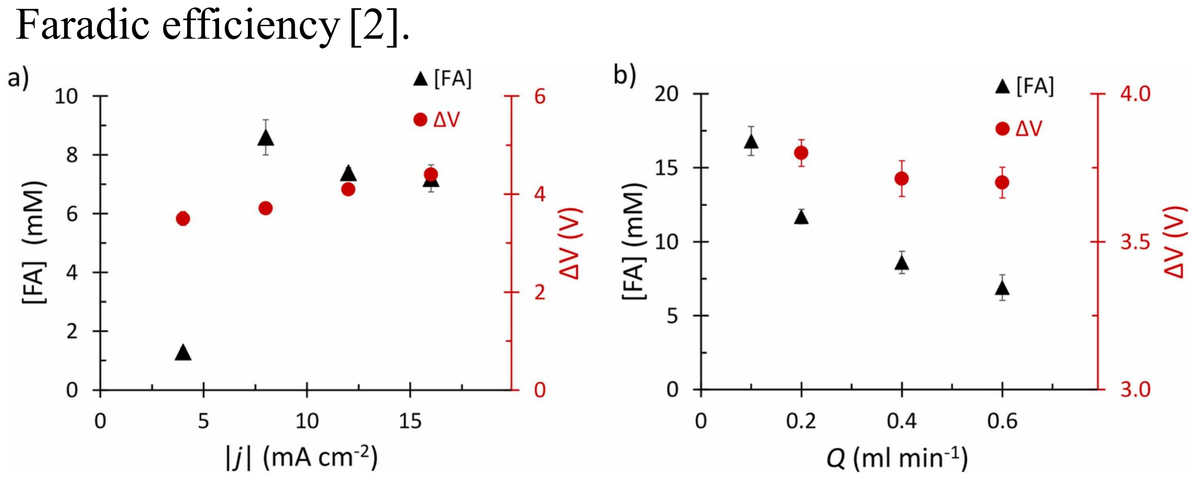

Figure 2. Effect of Q at 0.4 mL min^{-1} (Fig. 2a) and of j at – 8 mA cm^{-2} (Fig. 2b) on the reduction of CO_2 to FA.

MATERIALS AND METHODS

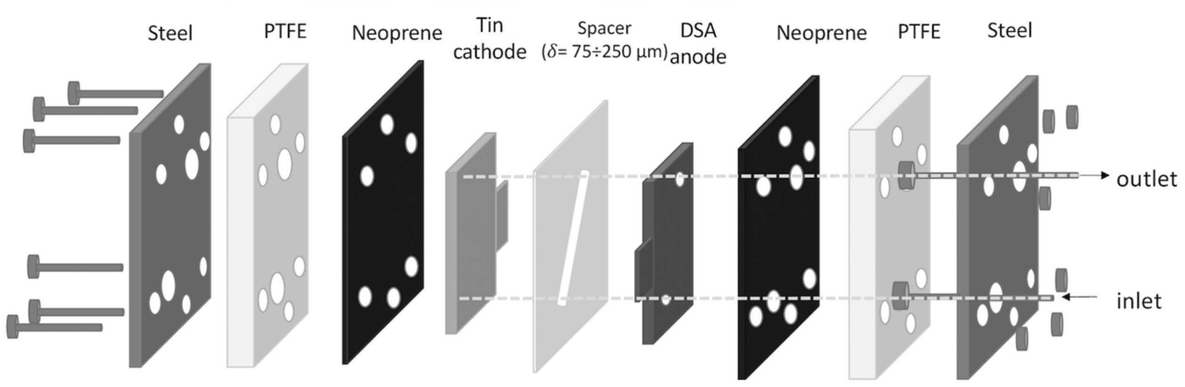

Figure 3. Schematic view of the microelectrochemical cell.

The microdevice was an undivided filter press flow cell from ElectroCell AB with proper modifications equipped with one or more PTFE spacers with an overall nominal thickness h of 250, 120 and 75 μm [2].

CONCLUSIONS

An important effect of operating parameters, including current density, flow rate and inter-electrode distances (75–250 μm), on the electrochemical reduction process of CO_2 to FA was observed. It was observed that the use of h < 140 μm and the absence of supporting electrolyte resulted in an appreciable final FA concentration and a relatively low ΔV. The optimum results in terms of FA concentration, were reached using an inter-electrode distances of 120 μm, intermediate values of j (– 8 mA cm^{-2}), low Q (0.4 mL min^{-1}) and values of initial pH close to 3–4 [2].

[1] Leung, Dennis Y.C., et al. "An overview of current status of carbon dioxide capture and storage technologies." Renewable and Sustainable Energy Reviews 39 (2014): 426-443.
[2] Proietto, Federica, et al. "Conversion of CO2 to formic acid in a microfluidic electrochemical cell with and without supporting electrolyte." Journal of Environmental Chemical Engineering 12 (2024): 112472.

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