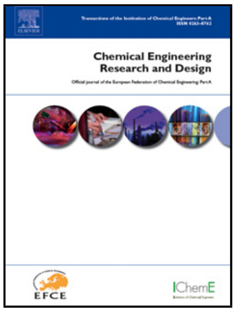

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Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: comparison with lead cathode

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Abstract

Electrochemical reduction has been pointed out as a promising method for CO_2 valorisation into useful chemicals. This paper studies the influence of key variables on the performance of an experimental system for continuous electro-reduction of CO_2 to formate, when a tin plate is used as working electrode. Particular emphasis is placed on comparing the performance of Sn and Pb as cathodes. As was previously found with Pb, the influence of current density ("j") using Sn was particularly noteworthy, and when j was raised up to a limit value of 8.5 mA cm^{-2}, important increases of the rate of formate production were observed at the expense of lowering the Faradaic efficiency. However, unlike what was found with Pb, the performance using Sn improved when the electrolyte flow rate/electrode area ratio was increased within the range studied (0.57-2.3 mL min^{-1} cm^{-2}). In this way, the use of Sn as cathode allowed achieving rates of formate production that were 25% higher than the maximum rates obtained with Pb, together with Faradaic efficiencies close to 70%, which were 15 points higher than those with Pb. These results reinforce the interest in Sn as electrode material in the electro-reduction of CO_2 to formate.

Keywords

Carbon dioxide; valorisation; electrochemical reduction; formate; continuous filter-press cell; Sn cathode

1. Introduction

Fossil fuels (i.e. oil, coal and natural gas) represented 81.1% of the total primary energy supply in the world in 2010, while renewable energies only accounted for 13.2% (IEA, 2011). Although the final objective for many countries is to phase out fossil fuels in heat and power production as well as in the transport sector (Toftegaard et al., 2010), prospects for the future indicate that the shift to renewable energy sources is slow and that the world energy supply will still depend on fossil fuels in the next decades.

The anthropogenic emissions of carbon dioxide (CO_2), which is the most significant greenhouse gas, are a major cause of global climate change (Figueroa et al., 2008), and they represent a complex challenge that needs to be tackled. Among the different alternatives that are being considered, the so-called “CO_2 valorisation” or “CO_2 chemical recycling” to convert CO_2 into useful and valuable products such as fuels or other derived hydrocarbons (Arakawa et al., 2001; Jiang et al., 2010; Mikkelsen et al., 2010; Quadrelli et al., 2011; Yu et al., 2008) appears as an innovative and attractive option, which has been regarded as a feasible and powerful new approach that is entering the stage of gradual practical implementation (Olah et al., 2009, 2011).

Particularly, electrochemical valorisation of CO_2 is receiving increasing attention over the last years. Several papers can be found in the literature that have reviewed different efforts in the study of CO_2 electro-reduction and have discussed mechanistic aspects and reaction pathways (Chaplin and Wragg, 2003; Gattrell et al., 2006; Jitaru et al., 1997; Jitaru, 2007; Lee et al., 2009; Spinner et al., 2012; Sánchez-Sánchez et al., 2001; Whipple and Kenis, 2010).

Valorisation of CO_2 by electrochemical reduction is based on the supply of electrical energy to establish a potential between two electrodes in order to allow CO_2 to be converted into reduced forms. Different authors have suggested that the electrochemical valorisation of CO_2 may be an excellent way of storing intermittent and unpredictable renewable energy, which can be used for supplying the electricity required for this process (Agarwal et al., 2011; Chen and Kanan, 2012; Narayanan et al., 2011; Olah et al., 2011; Prakash et al., 2013; Wang et al., 2013; Whipple et al., 2010). A negative public opinion to CO_2 storage, which has already been detected recently in the lack of social acceptance of some projects for storing captured CO_2, may hamper its implementation (Ashworth et al., 2012; Terwel and Daamen, 2012; Terwel et al., 2012; Upham and Roberts, 2011) and therefore may increase the interest in finding ways of converting captured CO_2 into useful products. Particularly, coupled to a renewable energy source such as wind or solar, electrochemical processes for CO_2 conversion could generate carbon neutral fuels or industrial chemicals that are conventionally derived from petroleum (Kuhl et al., 2012), and at the same time, could also allow the storage of electrical energy in chemical forms, which has been remarked as a key aspect for levelling the output from intermittent electricity sources such as wind and solar (Whipple and Kenis, 2010). Since electricity is difficult to store on a large scale, its production has to closely follow the demand and to adapt to fluctuations; however, renewable energies such as solar and wind are intermittent and not able to follow closely the demand (i.e. solar energy cannot be produced during the night or with cloudy weather, while wind does not blow constantly), so storage of electricity to balance fluctuations in demand and production cycles is considered to be essential for the use of renewable energies on a large scale (Olah et al., 2011; Prakash et al., 2013). In this way, it has been highlighted that if the electrochemical reduction of CO_2 to liquid chemical compounds could be made with high efficiencies, it could become a sustainable approach in the future for the production of liquid fuels, providing a high energy density means of storing renewable electricity as chemical energy (Gattrell et al., 2006; Kuhl et al., 2012; Narayanan et al., 2011; Olah et al., 2011; Prakash et al., 2013; Whipple et al., 2010).

In the electro-reduction of CO_2, the type of products, as well as the yield in which they can be obtained, are strongly dependent on different factors, emphasising the nature and form of the material used as cathode, the medium where the reaction occurs or the conditions of pressure and temperature (Hori et al., 1994; Jitaru et al., 1997; Jitaru, 2007; Sánchez-Sánchez et al., 2001). Among the number of useful products into which CO_2 can be electrochemically reduced, conversion to formic acid/ formate appears to have the best chance for the practical development of technical and economically viable processes (Oloman and Li, 2008). Apart from its different traditional industrial uses, including textile finishing or additive in animal feeds (Kirk-Othmer, 2004), a growing demand for formic acid in pharmaceutical synthesis and in paper and pulp production has been reported (Innocent et al., 2009). Furthermore, formic acid has been pointed out as one of the most promising candidate fuels for fuel cells (Rees and Compton, 2011; Yu and Pickup, 2008) and recently has been proposed as an optimal hydrogen carrier (Grasemann and Laurenczy, 2012; Prakash et al., 2013). However, formate/formic acid is currently mainly produced by the oxidation of hydrocarbons or by thermo-chemical processes based on the carbonylation of methanol or sodium hydroxide (Kirk-Othmer, 2004), which have negative environmental impacts (Li and Oloman, 2006) and are relatively expensive production processes (Agarwal et al., 2011).

As a consequence, the study of the electrochemical reduction of CO_2 to formate has attracted renewed and growing interest over the last years. Some studies have used fixed-bed reactors (Köleli et al., 2003; Köleli and Balun, 2004; Kwon and Lee, 2010) or divided H-type cells (Chen and Kanan, 2012; Kaneco et al., 1998, 1999; Li et al., 2012).

Nevertheless, several works in the literature have been focussed on parallel-plate or filter-press flow-by type cells (Agarwal et al., 2011; Akahori et al., 2004; Alvarez-Guerra et al., 2012; Innocent et al., 2009; Li and Oloman, 2005, 2006, 2007; Machunda et al., 2010, 2011; Narayanan et al., 2011; Subramanian et al., 2007; Whipple et al., 2010), under different working conditions and cathodes of very different nature, such as indium-impregnated lead wire (Akahori et al., 2004), lead-plated stainless steel woven mesh (Subramanian et al., 2007), tinned-copper mesh (Li and Oloman, 2005, 2006), tin particles (shots and granules) (Li and Oloman, 2007), lead plates (Alvarez-Guerra et al., 2012; Innocent et al., 2009), or metal catalysts (such as indium (Narayanan et al., 2011), lead (Machunda et al., 2010) or tin (Agarwal et al., 2011; Machunda et al., 2011; Whipple et al., 2010)) electrodeposited on different substrates. Apart from very recent investigations focussed on new gas diffusion electrodes (Li et al., 2012; Prakash et al., 2013), the CO_2 electrochemical valorisation to formate in continuous mode has been particularly studied in several works (Agarwal et al., 2011; Alvarez-Guerra et al., 2012; Li and Oloman, 2005, 2006, 2007; Subramanian et al., 2007), revealing the growing interest in this type of approach, but at the same time, emphasising that despite its great potential, there is the need for carrying on obtaining experimental evidence to guide the research efforts for developing and improving these processes.

Following previous studies of our research group using lead cathode (Alvarez-Guerra et al., 2012), the aim of this work is to analyse the influence of key variables like the current density and the electrolyte flow rate on the performance of an experimental system for continuous electro-reduction of CO_2 to formate, when a tin plate is used as working electrode in a filter-press electrochemical reactor. Special emphasis will be placed on comparing the performance of Sn plates with that of Pb plates previously reported (Alvarez-Guerra et al., 2012), and for this reason, the same approach was followed to carry out the analysis with Sn that will be presented in this paper, i.e. a 2^2 factorial design of experiments at different levels of current density and electrolyte flow rate, followed by subsequent more detailed studies of the influence of each of these variables on the performance of the process. These types of studies will allow the description of the system behaviour and can serve as a reference for the assessment of future advances.

2. Methods

In this work, the experimental laboratory system and operating conditions were the same as in our previous study using lead cathode (Alvarez-Guerra et al., 2012), with the only difference of using a tin plate (99.9% Sn, Amat Metalplast SA) as cathode. Details about the elements of the experimental set-up and about the methodology followed to carry out the experiments can be found in our previous work (Alvarez-Guerra et al., 2012). Briefly, the experimental laboratory system, whose core is a filter-press or parallel-plate type electrochemical cell (Micro Flow Cell, ElectroCell A/S), is represented in Figure 1. A Nafion 117 cation-exchange membrane divided the cell in two separated anodic and cathodic compartments. In this study, the working electrode was a tin plate and a Dimensionally Stable Anode DSA/O_2 plate (Ir-MMO (Mixed Metal Oxide) on Platinum, Electrocell A/S) was used as the counter-electrode, both electrodes with a surface area of 10 cm^2. A leak-free Ag/AgCl 3.4M KCl reference electrode was assembled in a PTFE frame of the cell very close to the surface of the working electrode. Following the same pre-treatment that was used in the study with Pb electrodes (Alvarez-Guerra et al., 2012), the Sn electrode was pre-treated before the start of each experiment with 11% wt HNO_3 for 1 min and then rinsed with plenty of ultra-pure water in an ultrasound bath for 5 min. An aqueous solution 0.45M $KHCO_3$ + 0.5M KCl, which was maintained saturated with CO_2 using constant bubbling throughout the experiment, was used as catholyte, and 1M KOH was used as anolyte.

(FIGURE 1 HERE)

Experiments were carried out in continuous mode with an operating time of 90 min, under room temperature and pressure, and at galvanostatic conditions with a potentiostat/galvanostat AutoLab PGSTAT 302N (Metrohm, Inc.) that was controlled with a computer using the General Purpose Electrochemical System (GPES) software. Samples were taken at different times (15, 30, 60 and 90 min) of operation and the average value of the concentrations of these samples was obtained for each experiment. Each sample was analysed in duplicate by Ion Chromatography (Dionex ICS 1100) provided with a AS9-HC column, using a solution of Na2CO3 (4.5 mM) as eluent, with a flow-rate of 1 mL/min and a pressure of around 2000 psi, to quantify the concentration of formate produced. As explained in our previous work (Alvarez-Guerra et al., 2012), considering the intrinsic variability associated with this type of electrochemical processes, at least two experiments were always performed for each of the points studied. In this way, standard deviations for the replicates of most of the points were below 5% of the average product concentration, with maximum deviations around 10%.

The rate of formate production and the Faradaic current efficiency for formate production were used to assess the performance of the process. The rate of formate production was expressed as the quantity of formate obtained per unit of cathode area and unit of time (i.e. mol m^{-2} s^{-1}). The Faradaic efficiency for a certain product is a figure of merit commonly used to assess the performance of an electrochemical process; it is defined as the yield based on the electrical charge passed during electrolysis (Pletcher and Walsh, 1990), or in other words, as the percentage of the total charge supplied that is used in forming that certain product.

3. Results and discussion

3.1. Factorial design of experiments at different current densities and flow/electrode area ratio

The effects of current density and electrolyte flow rate on the performance of the experimental laboratory-scale electro-reduction process to convert CO_2 into formate using Sn plate cathode were analysed with a 2^2 factorial design of experiments, following the same approach as that used in the previous study with Pb cathode (Alvarez-Guerra et al., 2012). Therefore, the variables current density (*j*) and "flow/area" ratio (*Q/A*, i.e. the feed flow rate used for the catholyte divided by the working electrode area, 10 cm^2), were studied in the same ranges: 2.5 – 22 mA cm^{-2} and 0.57 – 2.3 mL min^{-1} cm^{-2}, respectively. Three levels (low (-), medium (0) and high (+)) within these ranges were defined for each variable: 0.57, 1.44 and 2.3 mL min^{-1} cm^{-2} for *Q/A*, and 2.5, 12.25 and 22 mA cm^{-2} for *j*.

The results obtained in the different experiments carried out using a Sn plate as working electrode are summarised in Table 1. It is important to emphasise that, in each experiment, no significant changes with time were observed in the concentrations of the samples taken during the 90 min of operation. For each of the points studied, the deviations for these samples were below 10% of the average measured formate concentration reported. The statistical analysis of these factorial experiments was carried out using Minitab® 15 (Minitab Inc.) and MATLAB® 7.10 (MathWorks, Inc.) in a sequential way, as described in our previous work (Alvarez-Guerra et al., 2012): first only the high and low levels of the 2 factors (*j* and *Q/A*) were considered (i.e. 2^2 factorial design); then the centre point (0, 0) was included to test for curvature; and finally, the 3^2 combinations of the 2 factors at the 3 levels were analysed. With the aim of removing the influence of the absolute values in these analyses, both the factors (*j* and Q/A) and the responses (rate of formate production and Faradaic efficiency) were normalised in the range [-1, 1].

Table 1. Results of the factorial design of experiments using Sn cathode: levels of the variables (current density and flow/area ratio) and values obtained for the two responses (rate of formate production and Faradaic efficiency).

Point	Measured formate concentration (mg L^{-1})	Current density, *j*	Flow/area ratio, Q/A	Rate·10^4 (mol m^{-2} s^{-1})	Faradaic efficiency (%)	normalised rate [-1, +1] (-)	normalised Faradaic efficiency [-1, +1] (-)	Cathode potential vs. Ag/AgCl (V)	Cell potential (absolute value) (V)
		X_1 [a]	X_2 [b]	r	η	$\bar{r}$	$\bar{\eta}$	V_{cat}	V_{cell}
1	54.77	+	+	4.73	41.5	1.00	-0.28	-1.95	3.20
	49.37	+	+	4.26	37.4	0.76	-0.46	-1.80	3.15
2	39.36	-	-	0.83	64.1	-0.99	0.69	-1.39	2.07
	41.21	-	-	0.87	67.2	-0.97	0.82	-1.40	2.08
3	146.10	+	-	3.08	27.1	0.16	-0.90	-1.90	3.10
	133.33	+	-	2.81	24.7	0.02	-1.00	-1.88	3.11
4	9.41	-	+	0.81	62.7	-1.00	0.63	-1.45	2.13
	9.84	-	+	0.85	65.5	-0.98	0.75	-1.45	2.13
5	64.18	0	0	3.42	52.8	0.33	0.21	-1.70	2.64
	65.93	0	0	3.52	54.3	0.38	0.27	-1.72	2.66
6	71.70	+	0	3.82	33.5	0.54	-0.62	-1.86	3.10
	71.86	+	0	3.83	33.6	0.54	-0.62	-1.88	3.12
7	15.50	-	0	0.83	63.8	-0.99	0.67	-1.40	2.15
	15.85	-	0	0.85	65.2	-0.98	0.74	-1.42	2.15
8	47.49	0	+	4.10	63.3	0.68	0.65	-1.73	2.70
	53.61	0	+	4.63	71.4	0.95	1.00	-1.86	2.79
9	101.68	0	-	2.15	33.1	-0.32	-0.64	-1.77	2.68
	103.96	0	-	2.19	33.9	-0.29	-0.61	-1.88	2.76

[a] Levels for current density (mA cm^{-2}): 22 (+), 2.5 (-), 12.25 (0)
[b] Levels for flow/area ratio (mL min^{-1} cm^{-2}): 2.3 (+), 0.57 (-), 1.44 (0)

Table 2. Statistical analysis of the 2^2 factorial experiments with Sn cathode. $\overline{r}$ is the normalised rate of formate production and $\overline{\eta}$ is the normalised Faradaic efficiency.

Response	Current density, X_1			Flow/area ratio, X_2			Regression model: response = $\beta_0+\beta_1X_1+\beta_2X_2$			
	Main effect	Standard error	P*	Main effect	Standard error	P*	Coefficients (with 95% confidence bounds)			R^2
							β_0	β_1	β_2	
$\overline{r}$ (-)	1.472	0.094	0.001	0.389	0.094	0.095	-0.249 ±0.243	0.736 ±0.243	0.195 ±0.243	0.9284
$\overline{\eta}$ (-)	-1.379	0.078	0.000	0.257	0.078	0.162	0.030 ±0.201	-0.690 ±0.201	0.128 ±0.201	0.9415

***Significant ($\alpha=0.05$) if $P<0.05$**

Table 2 shows the results of the statistical analyses considering the low and high levels of the factors. As can be seen, current density had strong significant main effects on both rate and Faradaic efficiency, although with different sign. This means that the effect of increasing *j* from the low (2.5 mA cm^{-2}) to the high level studied (22 mA cm^{-2}) resulted in an increase of 1.47 in the value of rate normalised in the scale [-1, +1], but also made the efficiency to decrease in 1.38 within the coded scale. These main effects were similar, but greater, than the corresponding values obtained with Pb (1.316 for normalised rate and -1.295 for the normalised efficiency) (Alvarez-Guerra et al., 2012). It should also be emphasised that, as happened with Pb, the main effects of *Q/A* were positive on both factors but of minor magnitude that those of *j*. The main effect of *Q/A* on rate (0.389, Table 2) resulted almost identical to the corresponding value obtained in the study with Pb cathode (0.393) (Alvarez-Guerra et al., 2012). However, the effect of *Q/A* on efficiency that was obtained for Pb (0.476) almost doubled the value for Sn, which reveals the even lower influence of *Q/A* on $\overline{\eta}$ in the 2^2 factorial experiments with Sn.

Another way of expressing the results of a factorial design is in terms of a linear regression model (Montgomery, 1997). The β parameters that multiply the variables X_1

and X_2 (representing the factors current density and *Q/A* ratio, respectively) are included in Table 2. Looking at the values of these parameters of the regression model, the already mentioned influences can be confirmed. In this way, the great influence of *j* (positive on rate and negative on Faradaic efficiency) is revealed by the high values of their corresponding regression parameters, while the low β parameters that multiply *Q/A* indicated the much more limited influence of this variable.

Table 3. Statistical analysis of the 2^2 + centre point (0,0) factorial experiments with Sn cathode. $\bar{r}$ is the normalised rate of formate production and $\bar{\eta}$ is the normalised Faradaic efficiency.

Response	Current density, X_1			Flow/area ratio, X_2			Curvature	
	Main effect	Standard error	P*	Main effect	Standard error	P*	Center point	P*
$\bar{r}$ (-)	1.472	0.031	0.000	0.389	0.031	0.002	0.606	0.000
$\bar{\eta}$ (-)	-1.379	0.031	0.000	0.257	0.031	0.009	0.205	0.031

***Significant (α=0.05) if P<0.05**

Table 4. Regression models considering all the factorial experiments with Sn cathode, i.e. including the 3 levels of both factors X_1 (current density) and X_2 (flow/area ratio). $\bar{r}$ is the normalised rate of formate production and $\bar{\eta}$ is the normalised Faradaic efficiency.

Response	Coefficients ±95% confidence bounds for different terms					
	β_0	X_1 (β_1)	X_2 (β_2)	X_1X_2 (β_{12})	X_1X_1 (β_{11})	X_2X_2 (β_{22})
$\bar{r}$ (-)	0.324 ±0.220	0.746 ±0.120	0.316 ±0.120	0.200 ±0.147	-0.529 ±0.208	-0.052 ±0.208
$\bar{\eta}$ (-)	0.182 ±0.342	-0.681 ±0.187	0.327 ±0.187	0.161 ±0.229	-0.112 ±0.324	-0.053 ±0.324

Final regression models that only included coefficients of terms significant with 95% confidence:

$\bar{r} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2$

Response	β_0	β_1	β_2	β_{12}	β_{11}	R^2
$\bar{r}$ (-)	0.289 ±0.164	0.746 ±0.116	0.316 ±0.116	0.200 ±0.142	-0.529 ±0.201	0.9539

$\bar{\eta} = \beta_1 X_1 + \beta_2 X_2$

Response	β_1	β_2	R^2
$\bar{\eta}$ (-)	-0.681 ±0.183	0.327 ±0.183	0.8256

As done in the previous study with Pb, the results of the 2^2 factorial experiments were then analysed adding the centre point (0,0) in order to test for curvature. Table 3 reports the values of “centre point”, which measure the difference between the average of the centre-point response and the average of the factorial points (Montgomery, 1997). It can be seen that a large and significant value for curvature effect was obtained for rate, which suggests the existence of a non-linear behaviour, as also happened when using Pb as cathode. With Pb, curvature for Faradaic efficiency was very small (0.048) and statistically insignificant (Alvarez-Guerra et al., 2012); as shown in Table 3, in the case of Sn, curvature for $\bar{\eta}$ is statistically significant but smaller than for rate, which indicates the more limited influence of curvature in the response function $\bar{\eta}$ than in $\bar{r}$. Finally, regression models considering the 3 levels of both *j* and Q/A (i.e. all the factorial experiments, Table 1) were also calculated following the same approach as in the previous work with Pb. The regression models were successively fitted in such a way that those terms whose β parameters were not statistically significant with 95% confidence were eliminated in the following modelling equation, until obtaining models that only contained parameters with 95% confidence bounds that did not include the zero value (Alvarez-Guerra et al., 2012). Table 4 summarises the results that were obtained using Sn cathode. Regarding Faradaic efficiency, the important negative influence of *j* is represented by the high and negative value of β_1 parameter. It should be noted that the regression model considering the results of Faradaic efficiency from all the factorial experiments did not include other terms that were statistically significant apart from those corresponding to linear effects of *j* and *Q/A* (β_1 and $\beta_{2,}$ respectively). However, the R^2 achieved was low (0.826), which suggests that a better fit of these results would require the inclusion of other types of more complex mathematical expressions. However, the rate response function was satisfactorily modelled (R^2=0.954) with the expression obtained, as shown in Table 4. The influence of *j* in $\bar{r}$ is made again clear with the high positive influence of β_1, corresponding to the linear effect; moreover, the curvature detected can be especially modelled by the high and negative coefficient β_{11} that represents quadratic effects on rate associated with *j*.

3.2. Influence of the variables current density and flow/electrode area ratio in Sn cathode

In order to subsequently compare the behaviour of Sn and Pb plates as cathodes in our electrochemical system, the same detailed study of the influence of current density and catholyte flow/ electrode area ratio that had been done using Pb, was also done for Sn in this work. In this way, additional experiments were carried out at the intermediate value of the ranges of *Q/A* and *j* considered in the factorial study: on the one hand, using a constant flow/ area ratio of *Q/A* = 1.44 mL min^{-1} cm^{-2} and different current densities (*j*= 4.5, 6.5, 8.5, 10.5 and 14 mA cm^{-2}); and on the other hand, using a constant current density of 12.25 mA cm^{-2} and different flow/ area ratios (*Q/A*= 0.76, 1.00, 1.90 and 2.10 mL min^{-1} cm^{-2}).

The results of rate of formate production and Faradaic efficiency at all the different values of *Q/A* and *j* studied are summarised in Figure 2.

(FIGURE 2 HERE)

With respect to the influence of current density, it is interesting to note that increasing *j* from the lowest value 2.5 mA cm^{-2} to the medium level *j*= 12.25 mA cm^{-2} made the rate of formate formation to increase between 1.5 and 4 times depending on the level of *Q/A* ratio considered (i.e. rate increased 150% at *Q/A*= 0.57 mL min^{-1} cm^{-2}, 315% at 1.44 mL min^{-1} cm^{-2} and 425% at 2.3 mL min^{-1} cm^{-2}). Nevertheless, when *j* was further increased from 12.25 to 22 mA cm^{-2}, Figure 2 shows that such remarkable increases of rate were not observed; especially, for the middle and high *Q/A* studied, there were no significant difference between the rates obtained at current densities 12.25 and 22 mA cm^{-2}, but only resulted in falls of the % of Faradaic efficiency of 20 and 28 points. Focussing on the influence of *j* at *Q/A* = 1.44 mL min^{-1} cm^{-2}, it can clearly be seen in Figure 2 that the rate of formate production increased, nearly in a proportional way, when *j* was progressively increased from 2.5 up to 8.5 mA cm^{-2}. However, working at higher current densities did not make it possible to keep this linear growth; for all *j* studied higher than 8.5 mA cm^{-2}, the rate of formate obtained only varied in the narrow range between 3.47 $\cdot 10^{-4}$ and 3.83 $\cdot 10^{-4}$ mol m^{-2} s^{-1}, which represents maximum differences of approximately just 10%.

Regarding the influence of the catholyte flow / electrode area ratio, at the lowest level of *j* studied, no influence of *Q/A* was observed, since, as can be seen in Figure 2, the 3 points at *j*= 2.5 mA cm^{-2} were almost overlapped. However, the *Q/A* ratio did have an influence when working at the intermediate and high levels of *j* considered. In this way, at a certain *j*= 12.25 mA cm^{-2} or *j*= 22 mA cm^{-2}, increasing *Q/A* resulted in better performance of the process, both in terms of higher rate and Faradaic efficiency. This tendency can be clearly observed looking at the results of the experiments carried out at constant *j*= 12.25 mA cm^{-2} and different *Q/A* (Figure 2). The increase of efficiency and rate is strongly marked when *Q/A* was raised from 0.57 to 0.76 mL min^{-1} cm^{-2}. Although this rhythm of increase was not kept, in general higher formate rates and efficiencies were obtained when *Q/A* was increased. The highest values of rate and efficiency were achieved at *Q/A* = 2.3 mL min^{-1} cm^{-2}, which was the upper value of the range initially considered. Therefore, in order to test the performance beyond this limit, experiments at *Q/A* ratios higher than 2.3 were also carried out (i.e. at *Q/A*= 3, 3.5 and 4 mL min^{-1} cm^{-2}). The results have been included in Figure 2. As can be seen, further increase of *Q/A* did not give better results. It can be concluded that the experiments carried out at *Q/A* ratios above 2.3 mL min^{-1} cm^{-2} involved catholyte flows that resulted to be too high for our electrochemical system, which could cause effects of dragging that are detrimental to the performance of the process and could explain the lower rates of formate production and Faradaic efficiencies observed.

3.3. Comparison of performance with Sn and Pb cathodes

The graphs included in Figure 3 can help to compare the performance with Sn and Pb in terms of rate of formate production and Faradaic efficiency.

(FIGURE 3 HERE)

Regarding the influence of current density, both with Sn and Pb plates, increasing *j* from the low to the medium level caused the rate to increase between 2 and 4 times, although in general, as shown in Figure 3A, further increase of *j* did not result in higher rates of formation. The comparison of the results obtained with Pb and Sn at *Q/A*=1.44 mL min^{-1} cm^{-2} and different *j* allows detecting interesting differences (Figures 3A and 3B). It can be noticed in Figure 3A that when *j* was increased up to 10.5 mA cm^{-2} with the Pb cathode, the rate of formation increases linearly. As already mentioned, with Sn the proportional increase of rate with *j* is also observed, but in this case up to a current density of 8.5 mA cm^{-2}. It is especially noteworthy that at this value *j* = 8.5 mA cm^{-2}, the rate of formate production achieved with Sn resulted to be 40% higher than the corresponding rate obtained with Pb at this *j* (Figure 3A). Moreover, as can be seen in Figure 3B, and differently from Pb, when *j* was gradually increased using Sn between 4.5 and this limit value of 8.5 mA cm^{-2}, the observed Faradaic efficiency kept around 80%, which was higher than the value of 57% obtained at the limit *j* using Pb. However, a look together at Figures 3A and 3B confirms that, both with Pb and Sn, continuing increasing the current density (i.e. continuing increasing the supply of charge for the electro-reduction) above the corresponding certain limits (10.5 mA cm^{-2} with Pb and 8.5 mA cm^{-2} with Sn) did not raise the rate of formate production but only caused the Faradaic efficiency to fall noticeably. The interpretation of these results could be that the excess of electric charge supplied above these limits would not be employed in obtaining more amount of the desired product (formate), but instead, it would be used in other competitive reactions like the formation of $H_{2.}$ Therefore, this explained the decrease in Faradaic efficiencies observed. The observation of maximum current densities above which Faradaic efficiency decreased and rate did not improve, as has also been suggested in studies of photoelectrochemical reduction of CO_2, could be attributed to the limited solubility of CO_2 in water at standard pressures and its transport limitations (Kumar et al. 2012).

Figures 3C and 3D are useful to compare the influence of *Q/A* in the Pb and Sn cathode. At the low level of *j* studied (2.5 mA cm^{-2}), the influence of the *Q/A* ratio on the rate of formate production resulted to be very limited, especially using Sn (Figure 3C). At higher current densities, increasing the flow from the low to the medium level gave higher rates both in Sn and Pb, but further increase of *Q/A* involved different behaviour of the metals. This situation is especially noticeable in the experiments carried out at a same current density (i.e. *j*= 12.25 mA cm^{-2}) and various *Q/A* ratios. Working at higher *Q/A* ratios means that a higher amount of catholyte is made available per unit of time and of electrode area. This should involve improving the supply of mass for the reaction, and therefore, reducing mass transport limitations, which had been identified in the literature as one of the challenges to be overcome in these types of electrochemical processes (Lee et al., 2009; Oloman and Li, 2008; Subramanian et al., 2007; Sánchez-Sánchez et al., 2001). However, in the study with Pb plate, it was found that increasing the catholyte flow to overcome mass transport limitations only had beneficial effects for the lowest *Q/A* ratios (i.e. rate and efficiency only increased when *Q/A* was raised from 0.57 to 0.76 mL min^{-1} cm^{-2}), but further increase of *Q/A* did not result in better performance of the process, which was attributed to the fact that in such conditions the reaction to produce formate could be limited by other aspects, like adsorption equilibria in the lead cathode surface (Alvarez-Guerra et al., 2012). However, the results of the same analysis (working at *j*= 12.25 mA cm^{-2} and different *Q/A* ratios) using Sn plate cathode revealed differences with respect to the results obtained using Pb. As Figures 3C and 3D show, and unlike what was observed with Pb, using Sn cathode the performance generally improved when increasing *Q/A* ratios within the range studied (0.57- 2.3 mL min^{-1} cm^{-2}); in fact, the best result was obtained at 2.3 mL min^{-1} cm^{-2}. Therefore, it can be concluded that while working with Pb cathode at catholyte flow rates higher than a third of the maximum value of the range studied did not improve the performance (Alvarez-Guerra et al., 2012), this limitation was not found working with Sn cathode within the same Q/A range, which allowed achieving (working at the same *j*= 12.25 mA cm^{-2}) a formate rate production 25% higher than the best obtained using Pb, with a Faradaic efficiency 14 points higher in percentage.

Finally, it is worth comparing the behaviour of Pb and Sn cathodes in terms of the combination of rate of production and Faradaic efficiency. Working at the lowest current density studied, it can be stated that Pb had better performance than Sn. At *j*= 2.5 mA cm^{-2}, while with Sn the rates of formate production were $0.8 \cdot 10^{-4}$ mol m^{-2} s^{-1} with efficiencies of around 64% (Figure 2), using Pb it was possible to achieve an experimental point that combined a higher rate of $1.1 \cdot 10^{-4}$ mol m^{-2} s^{-1} and almost 87% of Faradaic efficiency (Alvarez-Guerra et al., 2012). However, at higher current densities, Sn gave better results than Pb in terms of points that combined both high rate and high efficiency. As can be seen in Figure 3, the use of Sn allowed achieving a rate of around $3.5 \cdot 10^{-4}$ mol m^{-2} s^{-1} with an efficiency of almost 80%. This rate is very similar to the maximum value obtained with Pb, but as can also be noticed in Figure 3, this maximum rate with Pb was achieved with an efficiency of near 60% (Alvarez-Guerra et al., 2012), which is 20 points lower than using Sn. Finally, it is also important to emphasise that a great advantage of Sn was that it allowed finding experimental conditions that gave simultaneously a rate of $4.4 \cdot 10^{-4}$ mol m^{-2} s^{-1} (25% higher than the best rates obtained with Pb) together with a Faradaic efficiency of around 70%. Therefore, it can be concluded that in the electrochemical system for CO_2 conversion into formate under study, Sn plates outperformed Pb plates as cathodes in terms of making it possible to work at conditions that combined higher rates of product formation with higher efficiencies than with Pb.

4. Conclusions

This paper presents new experimental results on the influence of key variables like the current density and electrolyte flow rate on the performance of a continuous electro-reduction process to convert CO_2 into formate in aqueous solutions under ambient conditions, when using a tin plate as cathode in a filter-press type electrochemical cell. Moreover, this study particularly focuses on comparing the performance of Sn plate with previous results obtained in our research group using Pb plate as cathode in the same experimental system (Alvarez-Guerra et al., 2012).

The analysis of the factorial design of experiments has allowed the quantification of the influence of j and Q/A. Moreover, the experiments carried out with Sn at the intermediate level of Q/A studied (1.44 mL min^{-1} cm^{-2}) showed that the rate of formate production increased, almost in a proportional way, when j was increased from 2.5 up to a limit value of 8.5 mA cm^{-2}. Following a similar behaviour as Pb, further increase of j using Sn did not improve the rate and only drastically lowered the efficiency. However, the detailed analyses done in this work also revealed interesting differences in the performance of the process using Pb or Sn plate as working electrode. Particularly, these comparative analyses allowed concluding that the best experimental points in terms of combining high rate and high efficiency obtained with Sn plate cathodes outperformed those with Pb plate, since with Sn the rates of formate production were 25% higher and with efficiencies close to 70%, improving the value of around 55% that we previously found with Pb. These results reinforce the interest in Sn as electrode material for the electro-reduction of CO_2 to formate and they can be useful as a reference when assessing future efforts in the development of continuous electro-reduction processes for CO_2 valorisation. In this sense, further research focussed on the application of Sn in gas diffusion electrodes (GDEs) appears as a clear possibility for potentially overcoming current limitations of these processes. Additional great potential for improvement may be related to the nature of the solvent, using, for example, non-aqueous media like ionic liquids. However, despite some studies that stress its excellent potential to aid in the electro-reduction of CO_2 (Barrosse-Antle and Compton, 2009; Martindale and Compton, 2012), great research efforts are still required to fully explore how the use of ionic liquid as solvents can improve the performance of these processes.

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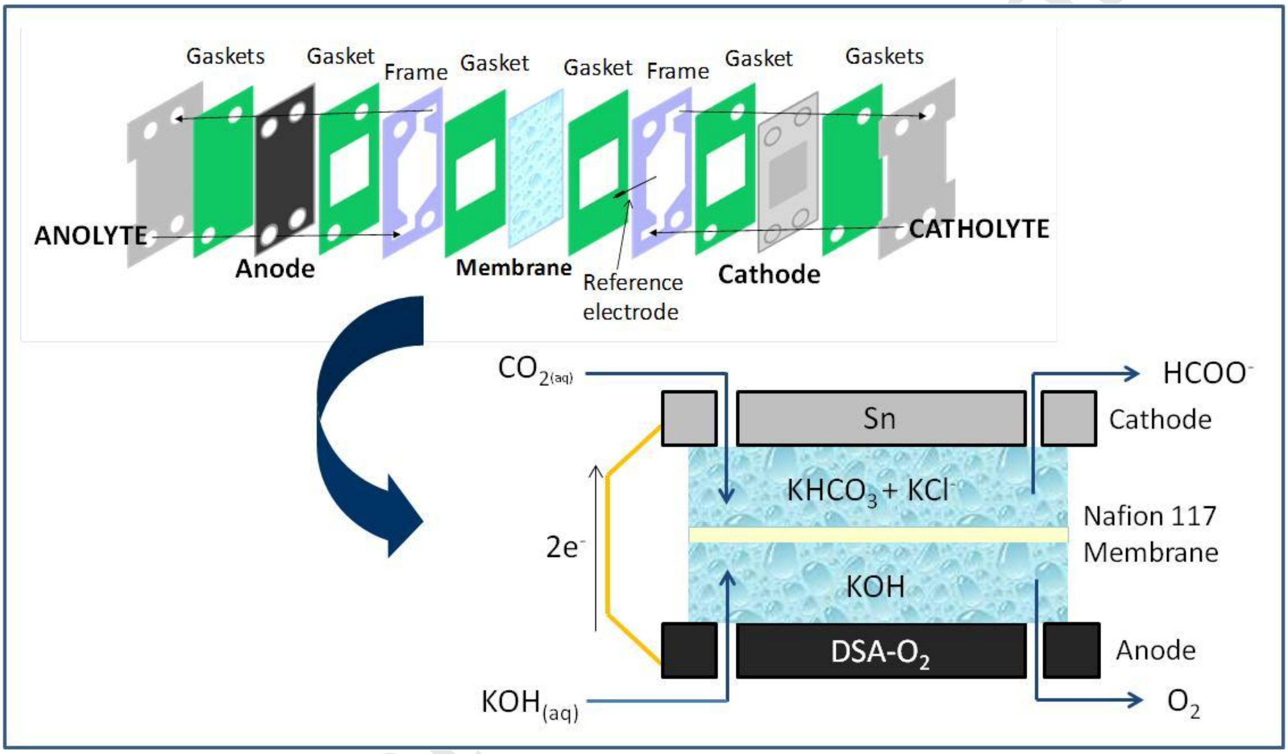
Graphical Abstract

“Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: comparison with lead cathode”



Highlights

“Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: comparison with lead cathode”

- The influence of key variables in a Sn cathode filter-press cell was studied
- The performance of Sn plate was compared with previous results using Pb
- As with Pb, the influence of current density using Sn was especially remarkable
- Results with Sn plate cathodes outperformed those with Pb plate
- These results reinforce the interest in Sn for CO_2 electrovalorisation to formate

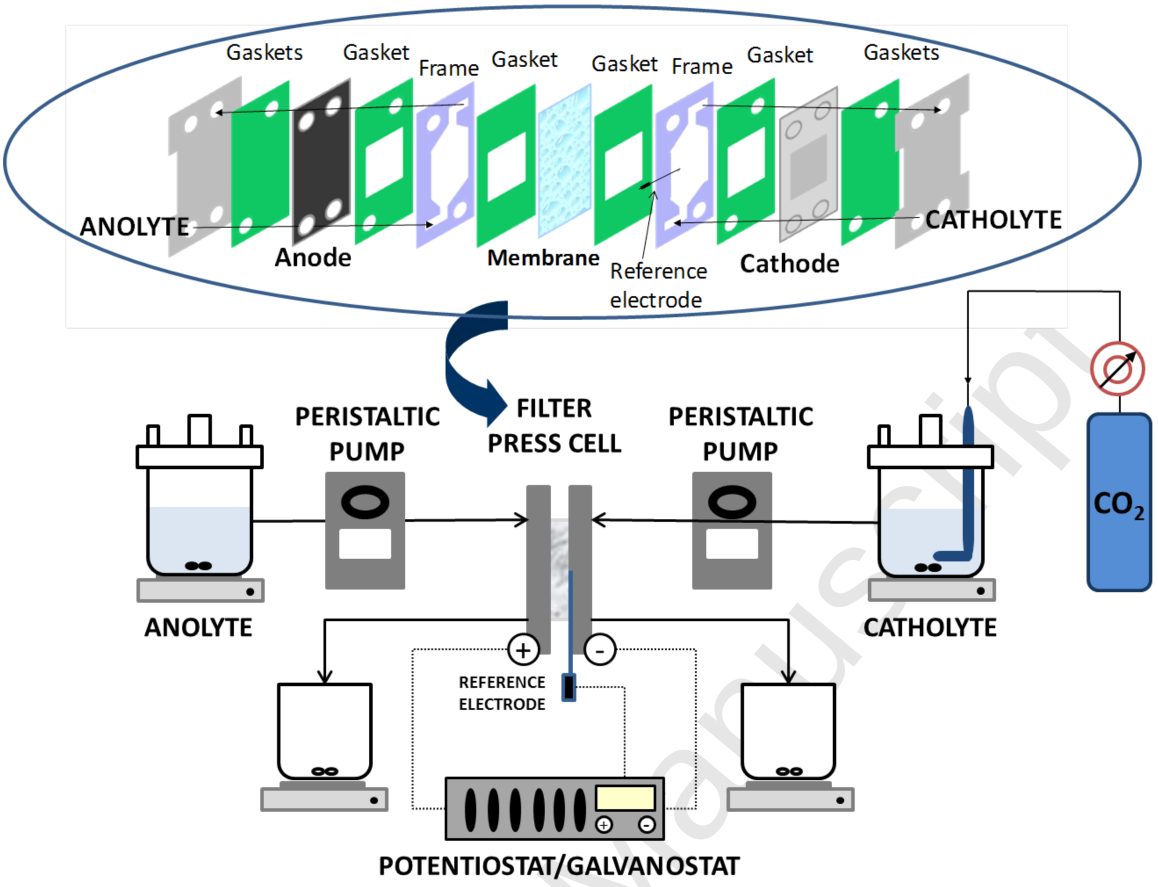


Figure 1. Diagram of the experimental set-up

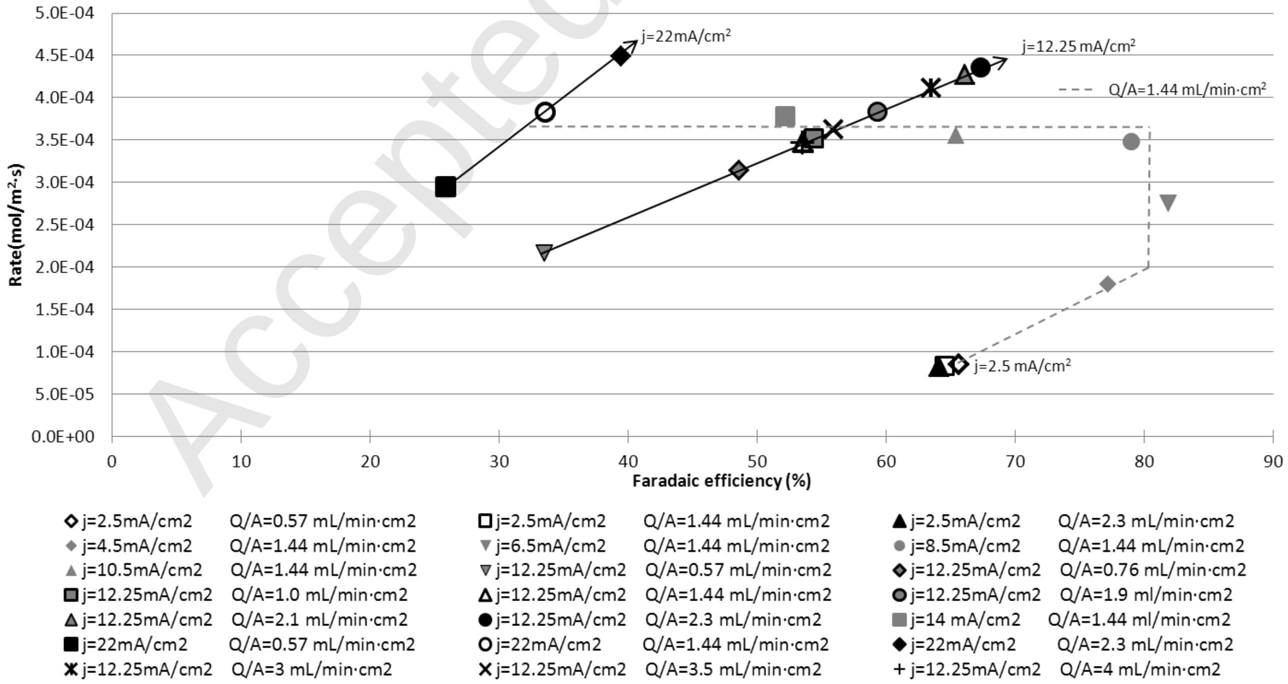


Figure 2. Relationship between the rate of formate production and Faradaic efficiency for formate at different flow/area ratios (Q/A) and current densities (*j*) using Sn cathode.

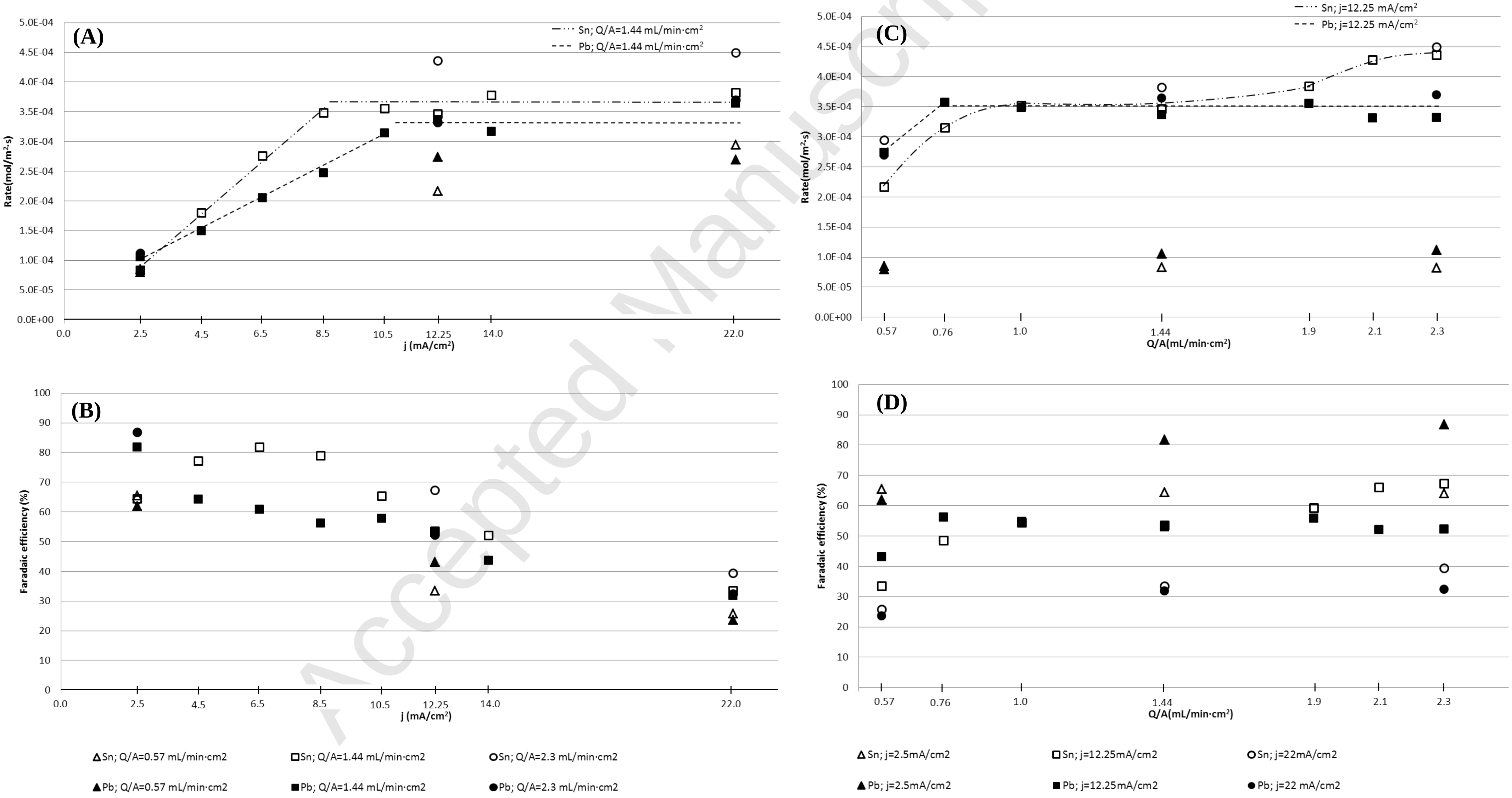


Figure 3. Comparison of the results obtained with Sn plate cathode and Pb plate cathode. (A) and (B): rates of formate production (A) and Faradaic efficiencies (B) vs current density (*j*). (C) and (D): rates of formate production (C) and Faradaic efficiencies (D) vs flow/area ratio (*Q/A*).