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1 **Continuous electrochemical reduction of carbon dioxide into formate**

2 **using a tin cathode: comparison with lead cathode**

3

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11 **Abstract**

12 Electrochemical reduction has been pointed out as a promising method for CO_2

13 valorisation into useful chemicals. This paper studies the influence of key variables on

14 the performance of an experimental system for continuous electro-reduction of CO_2 to

15 formate, when a tin plate is used as working electrode. Particular emphasis is placed on

16 comparing the performance of Sn and Pb as cathodes. As was previously found with Pb,

17 the influence of current density ("j") using Sn was particularly noteworthy, and when j

18 was raised up to a limit value of 8.5 mA cm^{-2}, important increases of the rate of formate

19 production were observed at the expense of lowering the Faradaic efficiency. However,

20 unlike what was found with Pb, the performance using Sn improved when the

21 electrolyte flow rate/electrode area ratio was increased within the range studied (0.57-

22 2.3 mL min^{-1} cm^{-2}). In this way, the use of Sn as cathode allowed achieving rates of

23 formate production that were 25% higher than the maximum rates obtained with Pb,

24 together with Faradaic efficiencies close to 70%, which were 15 points higher than

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25 those with Pb. These results reinforce the interest in Sn as electrode material in the

26 electro-reduction of CO_2 to formate.

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1. Introduction

34 Fossil fuels (i.e. oil, coal and natural gas) represented 81.1% of the total primary energy

35 supply in the world in 2010, while renewable energies only accounted for 13.2% (IEA,

36 2011). Although the final objective for many countries is to phase out fossil fuels in

37 heat and power production as well as in the transport sector (Toftegaard et al., 2010),

38 prospects for the future indicate that the shift to renewable energy sources is slow and

39 that the world energy supply will still depend on fossil fuels in the next decades.

40 The anthropogenic emissions of carbon dioxide (CO_2), which is the most significant

41 greenhouse gas, are a major cause of global climate change (Figueroa et al., 2008), and

42 they represent a complex challenge that needs to be tackled. Among the different

43 alternatives that are being considered, the so-called "CO_2 valorisation" or "CO_2

44 chemical recycling" to convert CO_2 into useful and valuable products such as fuels or

45 other derived hydrocarbons (Arakawa et al., 2001; Jiang et al., 2010; Mikkelsen et al.,

46 2010; Quadrelli et al., 2011; Yu et al., 2008) appears as an innovative and attractive

47 option, which has been regarded as a feasible and powerful new approach that is

48 entering the stage of gradual practical implementation (Olah et al., 2009, 2011).

49 Particularly, electrochemical valorisation of CO_2 is receiving increasing attention over

50 the last years. Several papers can be found in the literature that have reviewed different

51 efforts in the study of CO_2 electro-reduction and have discussed mechanistic aspects

52 and reaction pathways (Chaplin and Wragg, 2003; Gattrell et al., 2006; Jitaru et al.,

53 1997; Jitaru, 2007; Lee et al., 2009; Spinner et al., 2012; Sánchez-Sánchez et al., 2001;

54 Whipple and Kenis, 2010).

55 Valorisation of CO_2 by electrochemical reduction is based on the supply of electrical

56 energy to establish a potential between two electrodes in order to allow CO_2 to be

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57 converted into reduced forms. Different authors have suggested that the electrochemical

58 valorisation of CO_2 may be an excellent way of storing intermittent and unpredictable

59 renewable energy, which can be used for supplying the electricity required for this

60 process (Agarwal et al., 2011; Chen and Kanan, 2012; Narayanan et al., 2011; Olah et

61 al., 2011; Prakash et al., 2013; Wang et al., 2013; Whipple et al., 2010). A negative

62 public opinion to CO_2 storage, which has already been detected recently in the lack of

63 social acceptance of some projects for storing captured CO_2, may hamper its

64 implementation (Ashworth et al., 2012; Terwel and Daamen, 2012; Terwel et al., 2012;

65 Upham and Roberts, 2011) and therefore may increase the interest in finding ways of

66 converting captured CO_2 into useful products. Particularly, coupled to a renewable

67 energy source such as wind or solar, electrochemical processes for CO_2 conversion

68 could generate carbon neutral fuels or industrial chemicals that are conventionally

69 derived from petroleum (Kuhl et al., 2012), and at the same time, could also allow the

70 storage of electrical energy in chemical forms, which has been remarked as a key aspect

71 for levelling the output from intermittent electricity sources such as wind and solar

72 (Whipple and Kenis, 2010). Since electricity is difficult to store on a large scale, its

73 production has to closely follow the demand and to adapt to fluctuations; however,

74 renewable energies such as solar and wind are intermittent and not able to follow

75 closely the demand (i.e. solar energy cannot be produced during the night or with

76 cloudy weather, while wind does not blow constantly), so storage of electricity to

77 balance fluctuations in demand and production cycles is considered to be essential for

78 the use of renewable energies on a large scale (Olah et al., 2011; Prakash et al., 2013).

79 In this way, it has been highlighted that if the electrochemical reduction of CO_2 to liquid

80 chemical compounds could be made with high efficiencies, it could become a

81 sustainable approach in the future for the production of liquid fuels, providing a high

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82   energy density means of storing renewable electricity as chemical energy (Gattrell et al.,

83   2006; Kuhl et al., 2012; Narayanan et al., 2011; Olah et al., 2011; Prakash et al., 2013;

84   Whipple et al., 2010).

85   In the electro-reduction of CO_2, the type of products, as well as the yield in which they

86   can be obtained, are strongly dependent on different factors, emphasising the nature and

87   form of the material used as cathode, the medium where the reaction occurs or the

88   conditions of pressure and temperature (Hori et al., 1994; Jitaru et al., 1997; Jitaru,

89   2007; Sánchez-Sánchez et al., 2001). Among the number of useful products into which

90   CO_2 can be electrochemically reduced, conversion to formic acid/ formate appears to

91   have the best chance for the practical development of technical and economically viable

92   processes (Oloman and Li, 2008). Apart from its different traditional industrial uses,

93   including textile finishing or additive in animal feeds (Kirk-Othmer, 2004), a growing

94   demand for formic acid in pharmaceutical synthesis and in paper and pulp production

95   has been reported (Innocent et al., 2009). Furthermore, formic acid has been pointed out

96   as one of the most promising candidate fuels for fuel cells (Rees and Compton, 2011;

97   Yu and Pickup, 2008) and recently has been proposed as an optimal hydrogen carrier

98   (Grasemann and Laurenczy, 2012; Prakash et al., 2013). However, formate/formic acid

99   is currently mainly produced by the oxidation of hydrocarbons or by thermo-chemical

100   processes based on the carbonylation of methanol or sodium hydroxide (Kirk-Othmer,

101   2004), which have negative environmental impacts (Li and Oloman, 2006) and are

102   relatively expensive production processes (Agarwal et al., 2011).

103   As a consequence, the study of the electrochemical reduction of CO_2 to formate has

104   attracted renewed and growing interest over the last years. Some studies have used

105   fixed-bed reactors (Köleli et al., 2003; Köleli and Balun, 2004; Kwon and Lee, 2010) or

106   divided H-type cells (Chen and Kanan, 2012; Kaneco et al., 1998, 1999; Li et al., 2012).

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107   Nevertheless, several works in the literature have been focussed on parallel-plate or

108   filter-press flow-by type cells (Agarwal et al., 2011; Akahori et al., 2004; Alvarez-

109   Guerra et al., 2012; Innocent et al., 2009; Li and Oloman, 2005, 2006, 2007; Machunda

110   et al., 2010, 2011; Narayanan et al., 2011; Subramanian et al., 2007; Whipple et al.,

111   2010), under different working conditions and cathodes of very different nature, such as

112   indium-impregnated lead wire (Akahori et al., 2004), lead-plated stainless steel woven

113   mesh (Subramanian et al., 2007), tinned-copper mesh (Li and Oloman, 2005, 2006), tin

114   particles (shots and granules) (Li and Oloman, 2007), lead plates (Alvarez-Guerra et al.,

115   2012; Innocent et al., 2009), or metal catalysts (such as indium (Narayanan et al., 2011),

116   lead (Machunda et al., 2010) or tin (Agarwal et al., 2011; Machunda et al., 2011;

117   Whipple et al., 2010)) electrodeposited on different substrates. Apart from very recent

118   investigations focussed on new gas diffusion electrodes (Li et al., 2012; Prakash et al.,

119   2013), the CO_2 electrochemical valorisation to formate in continuous mode has been

120   particularly studied in several works (Agarwal et al., 2011; Alvarez-Guerra et al., 2012;

121   Li and Oloman, 2005, 2006, 2007; Subramanian et al., 2007), revealing the growing

122   interest in this type of approach, but at the same time, emphasising that despite its great

123   potential, there is the need for carrying on obtaining experimental evidence to guide the

124   research efforts for developing and improving these processes.

125   Following previous studies of our research group using lead cathode (Alvarez-Guerra et

126   al., 2012), the aim of this work is to analyse the influence of key variables like the

127   current density and the electrolyte flow rate on the performance of an experimental

128   system for continuous electro-reduction of CO_2 to formate, when a tin plate is used as

129   working electrode in a filter-press electrochemical reactor. Special emphasis will be

130   placed on comparing the performance of Sn plates with that of Pb plates previously

131   reported (Alvarez-Guerra et al., 2012), and for this reason, the same approach was

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132 followed to carry out the analysis with Sn that will be presented in this paper, i.e. a 2^2

133 factorial design of experiments at different levels of current density and electrolyte flow

134 rate, followed by subsequent more detailed studies of the influence of each of these

135 variables on the performance of the process. These types of studies will allow the

136 description of the system behaviour and can serve as a reference for the assessment of

137 future advances.

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140 **2. Methods**

141 In this work, the experimental laboratory system and operating conditions were the

142 same as in our previous study using lead cathode (Alvarez-Guerra et al., 2012), with the

143 only difference of using a tin plate (99.9% Sn, Amat Metalplast SA) as cathode. Details

144 about the elements of the experimental set-up and about the methodology followed to

145 carry out the experiments can be found in our previous work (Alvarez-Guerra et al.,

146 2012). Briefly, the experimental laboratory system, whose core is a filter-press or

147 parallel-plate type electrochemical cell (Micro Flow Cell, ElectroCell A/S), is

148 represented in Figure 1. A Nafion 117 cation-exchange membrane divided the cell in

149 two separated anodic and cathodic compartments. In this study, the working electrode

150 was a tin plate and a Dimensionally Stable Anode DSA/O_2 plate (Ir-MMO (Mixed

151 Metal Oxide) on Platinum, Electrocell A/S) was used as the counter-electrode, both

152 electrodes with a surface area of 10 cm^2. A leak-free Ag/AgCl 3.4M KCl reference

153 electrode was assembled in a PTFE frame of the cell very close to the surface of the

154 working electrode. Following the same pre-treatment that was used in the study with Pb

155 electrodes (Alvarez-Guerra et al., 2012), the Sn electrode was pre-treated before the

156 start of each experiment with 11% wt HNO_3 for 1 min and then rinsed with plenty of

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157   ultra-pure water in an ultrasound bath for 5 min. An aqueous solution 0.45M $KHCO_3$ +

158   0.5M KCl, which was maintained saturated with CO_2 using constant bubbling

159   throughout the experiment, was used as catholyte, and 1M KOH was used as anolyte.

160

161   (FIGURE 1 HERE)

162

163   Experiments were carried out in continuous mode with an operating time of 90 min,

164   under room temperature and pressure, and at galvanostatic conditions with a

165   potentiostat/galvanostat AutoLab PGSTAT 302N (Metrohm, Inc.) that was controlled

166   with a computer using the General Purpose Electrochemical System (GPES) software.

167   Samples were taken at different times (15, 30, 60 and 90 min) of operation and the

168   average value of the concentrations of these samples was obtained for each experiment.

169   Each sample was analysed in duplicate by Ion Chromatography (Dionex ICS 1100)

170   provided with a AS9-HC column, using a solution of Na2CO3 (4.5 mM) as eluent, with

171   a flow-rate of 1 mL/min and a pressure of around 2000 psi, to quantify the

172   concentration of formate produced. As explained in our previous work (Alvarez-Guerra

173   et al., 2012), considering the intrinsic variability associated with this type of

174   electrochemical processes, at least two experiments were always performed for each of

175   the points studied. In this way, standard deviations for the replicates of most of the

176   points were below 5% of the average product concentration, with maximum deviations

177   around 10%.

178   The rate of formate production and the Faradaic current efficiency for formate

179   production were used to assess the performance of the process. The rate of formate

180   production was expressed as the quantity of formate obtained per unit of cathode area

181   and unit of time (i.e. mol m^{-2} s^{-1}). The Faradaic efficiency for a certain product is a

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182 figure of merit commonly used to assess the performance of an electrochemical process;

183 it is defined as the yield based on the electrical charge passed during electrolysis

184 (Pletcher and Walsh, 1990), or in other words, as the percentage of the total charge

185 supplied that is used in forming that certain product.

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188 **3. Results and discussion**

189

190 **3.1. Factorial design of experiments at different current densities and**

191 **flow/electrode area ratio**

192 The effects of current density and electrolyte flow rate on the performance of the

193 experimental laboratory-scale electro-reduction process to convert CO_2 into formate

194 using Sn plate cathode were analysed with a 2^2 factorial design of experiments,

195 following the same approach as that used in the previous study with Pb cathode

196 (Alvarez-Guerra et al., 2012). Therefore, the variables current density (j) and

197 "flow/area" ratio (Q/A, i.e. the feed flow rate used for the catholyte divided by the

198 working electrode area, 10 cm^2), were studied in the same ranges: $2.5 – 22$ mA cm^{-2} and

199 $0.57 – 2.3$ mL min^{-1} cm^{-2}, respectively. Three levels (low (-), medium (0) and high (+))

200 within these ranges were defined for each variable: 0.57, 1.44 and 2.3 mL min^{-1} cm^{-2} for

201 Q/A, and 2.5, 12.25 and 22 mA cm^{-2} for j.

202 The results obtained in the different experiments carried out using a Sn plate as working

203 electrode are summarised in Table 1. It is important to emphasise that, in each

204 experiment, no significant changes with time were observed in the concentrations of the

205 samples taken during the 90 min of operation. For each of the points studied, the

206 deviations for these samples were below 10% of the average measured formate

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207　concentration reported. The statistical analysis of these factorial experiments was

208　carried out using Minitab® 15 (Minitab Inc.) and MATLAB® 7.10 (MathWorks, Inc.) in

209　a sequential way, as described in our previous work (Alvarez-Guerra et al., 2012): first

210　only the high and low levels of the 2 factors (j and Q/A) were considered (i.e. 2^2

211　factorial design); then the centre point (0, 0) was included to test for curvature; and

212　finally, the 3^2 combinations of the 2 factors at the 3 levels were analysed. With the aim

213　of removing the influence of the absolute values in these analyses, both the factors (j

214　and Q/A) and the responses (rate of formate production and Faradaic efficiency) were

215　normalised in the range [-1, 1].

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217 **Table 1. Results of the factorial design of experiments using Sn cathode: levels of the variables**
218 **(current density and flow/area ratio) and values obtained for the two responses (rate of formate**
219 **production and Faradaic efficiency).**
220

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

221 ^{a} **Levels for current density (mA cm^{-2}): 22 (+), 2.5 (-), 12.25 (0)**
222 ^{b} **Levels for flow/area ratio (mL min^{-1} cm^{-2}): 2.3 (+), 0.57 (-), 1.44 (0)**
223

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225 **Table 2. Statistical analysis of the 2^2 factorial experiments with Sn cathode. $\bar{r}$ is the normalised rate**

226 **of formate production and $\bar{\eta}$ is the normalised Faradaic efficiency.**

Response	Current density, X_1			Flow/area ratio, X_2			Regression model: response = $\beta_0 + \beta_1 X_1 + \beta_2 X_2$			
	Main effect	Standard error	P*	Main effect	Standard error	P*	Coefficients (with 95% confidence bounds)			R^2
							β_0	β_1	β_2	
$\bar{r}$ (-)	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
$\bar{\eta}$ (-)	-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

227

228 ***Significant (α=0.05) if P<0.05**

229

230 Table 2 shows the results of the statistical analyses considering the low and high levels

231 of the factors. As can be seen, current density had strong significant main effects on

232 both rate and Faradaic efficiency, although with different sign. This means that the

233 effect of increasing j from the low (2.5 mA cm^{-2}) to the high level studied (22 mA cm^{-2})

234 resulted in an increase of 1.47 in the value of rate normalised in the scale [-1, +1], but

235 also made the efficiency to decrease in 1.38 within the coded scale. These main effects

236 were similar, but greater, than the corresponding values obtained with Pb (1.316 for

237 normalised rate and -1.295 for the normalised efficiency) (Alvarez-Guerra et al., 2012).

238 It should also be emphasised that, as happened with Pb, the main effects of Q/A were

239 positive on both factors but of minor magnitude that those of j. The main effect of Q/A

240 on rate (0.389, Table 2) resulted almost identical to the corresponding value obtained in

241 the study with Pb cathode (0.393) (Alvarez-Guerra et al., 2012). However, the effect of

242 Q/A on efficiency that was obtained for Pb (0.476) almost doubled the value for Sn,

243 which reveals the even lower influence of Q/A on $\bar{\eta}$ in the 2^2 factorial experiments with

244 Sn.

245 Another way of expressing the results of a factorial design is in terms of a linear

246 regression model (Montgomery, 1997). The β parameters that multiply the variables X_1

12

247 and X_2 (representing the factors current density and *Q/A* ratio, respectively) are included

248 in Table 2. Looking at the values of these parameters of the regression model, the

249 already mentioned influences can be confirmed. In this way, the great influence of *j*

250 (positive on rate and negative on Faradaic efficiency) is revealed by the high values of

251 their corresponding regression parameters, while the low β parameters that multiply *Q/A*

252 indicated the much more limited influence of this variable.

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

	Current density, X_1			Flow/area ratio, X_2			Curvature	
Response	**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

255
256 ***Significant (α=0.05) if P<0.05**

257

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

Response	**Coefficients ±95% confidence bounds for different terms**					
	β_0	$X_1 (\beta_1)$	$X_2 (\beta_2)$	$X_1X_2 (\beta_{12})$	$X_1X_1 (\beta_{11})$	$X_2X_2 (\beta_{22})$
$\bar{r}$ (-)	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:					
	$\bar{r} = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_{12}X_1X_2 + \beta_{11}X_1^2$					
	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
	$\bar{\eta} = \beta_1X_1 + \beta_2X_2$					
	β_1	β_2				R^2
$\bar{\eta}$ (-)	-0.681 ±0.183	0.327 ±0.183				0.8256

13

261

262   As done in the previous study with Pb, the results of the 2^2 factorial experiments were

263   then analysed adding the centre point (0,0) in order to test for curvature. Table 3 reports

264   the values of "centre point", which measure the difference between the average of the

265   centre-point response and the average of the factorial points (Montgomery, 1997). It can

266   be seen that a large and significant value for curvature effect was obtained for rate,

267   which suggests the existence of a non-linear behaviour, as also happened when using Pb

268   as cathode. With Pb, curvature for Faradaic efficiency was very small (0.048) and

269   statistically insignificant (Alvarez-Guerra et al., 2012); as shown in Table 3, in the case

270   of Sn, curvature for $\bar{\eta}$ is statistically significant but smaller than for rate, which

271   indicates the more limited influence of curvature in the response function $\bar{\eta}$ than in $\bar{r}$.

272   Finally, regression models considering the 3 levels of both j and Q/A (i.e. all the

273   factorial experiments, Table 1) were also calculated following the same approach as in

274   the previous work with Pb. The regression models were successively fitted in such a

275   way that those terms whose β parameters were not statistically significant with 95%

276   confidence were eliminated in the following modelling equation, until obtaining models

277   that only contained parameters with 95% confidence bounds that did not include the

278   zero value (Alvarez-Guerra et al., 2012). Table 4 summarises the results that were

279   obtained using Sn cathode. Regarding Faradaic efficiency, the important negative

280   influence of j is represented by the high and negative value of β_1 parameter. It should be

281   noted that the regression model considering the results of Faradaic efficiency from all

282   the factorial experiments did not include other terms that were statistically significant

283   apart from those corresponding to linear effects of j and Q/A (β_1 and β_2, respectively).

284   However, the R^2 achieved was low (0.826), which suggests that a better fit of these

285   results would require the inclusion of other types of more complex mathematical

14

286 expressions. However, the rate response function was satisfactorily modelled

287 (R^2=0.954) with the expression obtained, as shown in Table 4. The influence of j in $\bar{r}$ is

288 made again clear with the high positive influence of β_1, corresponding to the linear

289 effect; moreover, the curvature detected can be especially modelled by the high and

290 negative coefficient β_{11} that represents quadratic effects on rate associated with j.

291

292

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

294 **cathode**

295 In order to subsequently compare the behaviour of Sn and Pb plates as cathodes in our

296 electrochemical system, the same detailed study of the influence of current density and

297 catholyte flow/ electrode area ratio that had been done using Pb, was also done for Sn in

298 this work. In this way, additional experiments were carried out at the intermediate value

299 of the ranges of Q/A and j considered in the factorial study: on the one hand, using a

300 constant flow/ area ratio of Q/A = 1.44 mL min^{-1} cm^{-2} and different current densities (j=

301 4.5, 6.5, 8.5, 10.5 and 14 mA cm^{-2}); and on the other hand, using a constant current

302 density of 12.25 mA cm^{-2} and different flow/ area ratios (Q/A= 0.76, 1.00, 1.90 and 2.10

303 mL min^{-1} cm^{-2}).

304 The results of rate of formate production and Faradaic efficiency at all the different

305 values of Q/A and j studied are summarised in Figure 2.

306

307 (FIGURE 2 HERE)

308

309 With respect to the influence of current density, it is interesting to note that increasing j

310 from the lowest value 2.5 mA cm^{-2} to the medium level j= 12.25 mA cm^{-2} made the rate

15

311 of formate formation to increase between 1.5 and 4 times depending on the level of Q/A

312 ratio considered (i.e. rate increased 150% at $Q/A = 0.57$ mL min^{-1} cm^{-2}, 315% at 1.44

313 mL min^{-1} cm^{-2} and 425% at 2.3 mL min^{-1} cm^{-2}). Nevertheless, when j was further

314 increased from 12.25 to 22 mA cm^{-2}, Figure 2 shows that such remarkable increases of

315 rate were not observed; especially, for the middle and high Q/A studied, there were no

316 significant difference between the rates obtained at current densities 12.25 and 22 mA

317 cm^{-2}, but only resulted in falls of the % of Faradaic efficiency of 20 and 28 points.

318 Focussing on the influence of j at $Q/A = 1.44$ mL min^{-1} cm^{-2}, it can clearly be seen in

319 Figure 2 that the rate of formate production increased, nearly in a proportional way,

320 when j was progressively increased from 2.5 up to 8.5 mA cm^{-2}. However, working at

321 higher current densities did not make it possible to keep this linear growth; for all j

322 studied higher than 8.5 mA cm^{-2}, the rate of formate obtained only varied in the narrow

323 range between $3.47 \cdot 10^{-4}$ and $3.83 \cdot 10^{-4}$ mol m^{-2} s^{-1}, which represents maximum

324 differences of approximately just 10%.

325

326 Regarding the influence of the catholyte flow / electrode area ratio, at the lowest level of

327 j studied, no influence of Q/A was observed, since, as can be seen in Figure 2, the 3

328 points at $j = 2.5$ mA cm^{-2} were almost overlapped. However, the Q/A ratio did have an

329 influence when working at the intermediate and high levels of j considered. In this way,

330 at a certain $j = 12.25$ mA cm^{-2} or $j = 22$ mA cm^{-2}, increasing Q/A resulted in better

331 performance of the process, both in terms of higher rate and Faradaic efficiency. This

332 tendency can be clearly observed looking at the results of the experiments carried out at

333 constant $j = 12.25$ mA cm^{-2} and different Q/A (Figure 2). The increase of efficiency and

334 rate is strongly marked when Q/A was raised from 0.57 to 0.76 mL min^{-1} cm^{-2}.

335 Although this rhythm of increase was not kept, in general higher formate rates and

16

336 efficiencies were obtained when Q/A was increased. The highest values of rate and

337 efficiency were achieved at $Q/A = 2.3$ mL min^{-1} cm^{-2}, which was the upper value of the

338 range initially considered. Therefore, in order to test the performance beyond this limit,

339 experiments at Q/A ratios higher than 2.3 were also carried out (i.e. at $Q/A= 3$, 3.5 and 4

340 mL min^{-1} cm^{-2}). The results have been included in Figure 2. As can be seen, further

341 increase of Q/A did not give better results. It can be concluded that the experiments

342 carried out at Q/A ratios above 2.3 mL min^{-1} cm^{-2} involved catholyte flows that resulted

343 to be too high for our electrochemical system, which could cause effects of dragging

344 that are detrimental to the performance of the process and could explain the lower rates

345 of formate production and Faradaic efficiencies observed.

346

347

348 **3.3. Comparison of performance with Sn and Pb cathodes**

349 The graphs included in Figure 3 can help to compare the performance with Sn and Pb in

350 terms of rate of formate production and Faradaic efficiency.

351

352 (FIGURE 3 HERE)

353

354 Regarding the influence of current density, both with Sn and Pb plates, increasing j

355 from the low to the medium level caused the rate to increase between 2 and 4 times,

356 although in general, as shown in Figure 3A, further increase of j did not result in higher

357 rates of formation. The comparison of the results obtained with Pb and Sn at Q/A=1.44

358 mL min^{-1} cm^{-2} and different j allows detecting interesting differences (Figures 3A and

359 3B). It can be noticed in Figure 3A that when j was increased up to 10.5 mA cm^{-2} with

360 the Pb cathode, the rate of formation increases linearly. As already mentioned, with Sn

17

361 the proportional increase of rate with j is also observed, but in this case up to a current

362 density of 8.5 mA cm^{-2}. It is especially noteworthy that at this value $j = 8.5$ mA cm^{-2},

363 the rate of formate production achieved with Sn resulted to be 40% higher than the

364 corresponding rate obtained with Pb at this j (Figure 3A). Moreover, as can be seen in

365 Figure 3B, and differently from Pb, when j was gradually increased using Sn between

366 4.5 and this limit value of 8.5 mA cm^{-2}, the observed Faradaic efficiency kept around

367 80%, which was higher than the value of 57% obtained at the limit j using Pb. However,

368 a look together at Figures 3A and 3B confirms that, both with Pb and Sn, continuing

369 increasing the current density (i.e. continuing increasing the supply of charge for the

370 electro-reduction) above the corresponding certain limits (10.5 mA cm^{-2} with Pb and 8.5

371 mA cm^{-2} with Sn) did not raise the rate of formate production but only caused the

372 Faradaic efficiency to fall noticeably. The interpretation of these results could be that

373 the excess of electric charge supplied above these limits would not be employed in

374 obtaining more amount of the desired product (formate), but instead, it would be used in

375 other competitive reactions like the formation of H_2. Therefore, this explained the

376 decrease in Faradaic efficiencies observed. The observation of maximum current

377 densities above which Faradaic efficiency decreased and rate did not improve, as has

378 also been suggested in studies of photoelectrochemical reduction of CO_2, could be

379 attributed to the limited solubility of CO_2 in water at standard pressures and its transport

380 limitations (Kumar et al. 2012).

381

382 Figures 3C and 3D are useful to compare the influence of Q/A in the Pb and Sn cathode.

383 At the low level of j studied (2.5 mA cm^{-2}), the influence of the Q/A ratio on the rate of

384 formate production resulted to be very limited, especially using Sn (Figure 3C). At

385 higher current densities, increasing the flow from the low to the medium level gave

18

386 higher rates both in Sn and Pb, but further increase of *Q/A* involved different behaviour

387 of the metals. This situation is especially noticeable in the experiments carried out at a

388 same current density (i.e. *j*= 12.25 mA cm^{-2}) and various *Q/A* ratios. Working at higher

389 *Q/A* ratios means that a higher amount of catholyte is made available per unit of time

390 and of electrode area. This should involve improving the supply of mass for the

391 reaction, and therefore, reducing mass transport limitations, which had been identified

392 in the literature as one of the challenges to be overcome in these types of

393 electrochemical processes (Lee et al., 2009; Oloman and Li, 2008; Subramanian et al.,

394 2007; Sánchez-Sánchez et al., 2001). However, in the study with Pb plate, it was found

395 that increasing the catholyte flow to overcome mass transport limitations only had

396 beneficial effects for the lowest *Q/A* ratios (i.e. rate and efficiency only increased when

397 *Q/A* was raised from 0.57 to 0.76 mL min^{-1} cm^{-2}), but further increase of *Q/A* did not

398 result in better performance of the process, which was attributed to the fact that in such

399 conditions the reaction to produce formate could be limited by other aspects, like

400 adsorption equilibria in the lead cathode surface (Alvarez-Guerra et al., 2012).

401 However, the results of the same analysis (working at *j*= 12.25 mA cm^{-2} and different

402 *Q/A* ratios) using Sn plate cathode revealed differences with respect to the results

403 obtained using Pb. As Figures 3C and 3D show, and unlike what was observed with Pb,

404 using Sn cathode the performance generally improved when increasing *Q/A* ratios

405 within the range studied (0.57- 2.3 mL min^{-1} cm^{-2}); in fact, the best result was obtained

406 at 2.3 mL min^{-1} cm^{-2}. Therefore, it can be concluded that while working with Pb cathode

407 at catholyte flow rates higher than a third of the maximum value of the range studied

408 did not improve the performance (Alvarez-Guerra et al., 2012), this limitation was not

409 found working with Sn cathode within the same Q/A range, which allowed achieving

19

410 (working at the same j= 12.25 mA cm^{-2}) a formate rate production 25% higher than the

411 best obtained using Pb, with a Faradaic efficiency 14 points higher in percentage.

412

413 Finally, it is worth comparing the behaviour of Pb and Sn cathodes in terms of the

414 combination of rate of production and Faradaic efficiency. Working at the lowest

415 current density studied, it can be stated that Pb had better performance than Sn. At j=

416 2.5 mA cm^{-2}, while with Sn the rates of formate production were $0.8 \cdot 10^{-4}$ mol m^{-2} s^{-1}

417 with efficiencies of around 64% (Figure 2), using Pb it was possible to achieve an

418 experimental point that combined a higher rate of $1.1 \cdot 10^{-4}$ mol m^{-2} s^{-1} and almost 87%

419 of Faradaic efficiency (Alvarez-Guerra et al., 2012). However, at higher current

420 densities, Sn gave better results than Pb in terms of points that combined both high rate

421 and high efficiency. As can be seen in Figure 3, the use of Sn allowed achieving a rate

422 of around $3.5 \cdot 10^{-4}$ mol m^{-2} s^{-1} with an efficiency of almost 80%. This rate is very

423 similar to the maximum value obtained with Pb, but as can also be noticed in Figure 3,

424 this maximum rate with Pb was achieved with an efficiency of near 60% (Alvarez-

425 Guerra et al., 2012), which is 20 points lower than using Sn. Finally, it is also important

426 to emphasise that a great advantage of Sn was that it allowed finding experimental

427 conditions that gave simultaneously a rate of $4.4 \cdot 10^{-4}$ mol m^{-2} s^{-1} (25% higher than the

428 best rates obtained with Pb) together with a Faradaic efficiency of around 70%.

429 Therefore, it can be concluded that in the electrochemical system for CO_2 conversion

430 into formate under study, Sn plates outperformed Pb plates as cathodes in terms of

431 making it possible to work at conditions that combined higher rates of product

432 formation with higher efficiencies than with Pb.

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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

21

460   potentially overcoming current limitations of these processes. Additional great potential

461   for improvement may be related to the nature of the solvent, using, for example, non-

462   aqueous media like ionic liquids. However, despite some studies that stress its excellent

463   potential to aid in the electro-reduction of CO_2 (Barrosse-Antle and Compton, 2009;

464   Martindale and Compton, 2012), great research efforts are still required to fully explore

465   how the use of ionic liquid as solvents can improve the performance of these processes.

466

467

468   **Acknowledgements**

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473   **References**

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26

Graphical Abstract

"**Continuous electrochemical reduction of carbon dioxide into formate using a tin**

cathode: comparison with lead cathode"
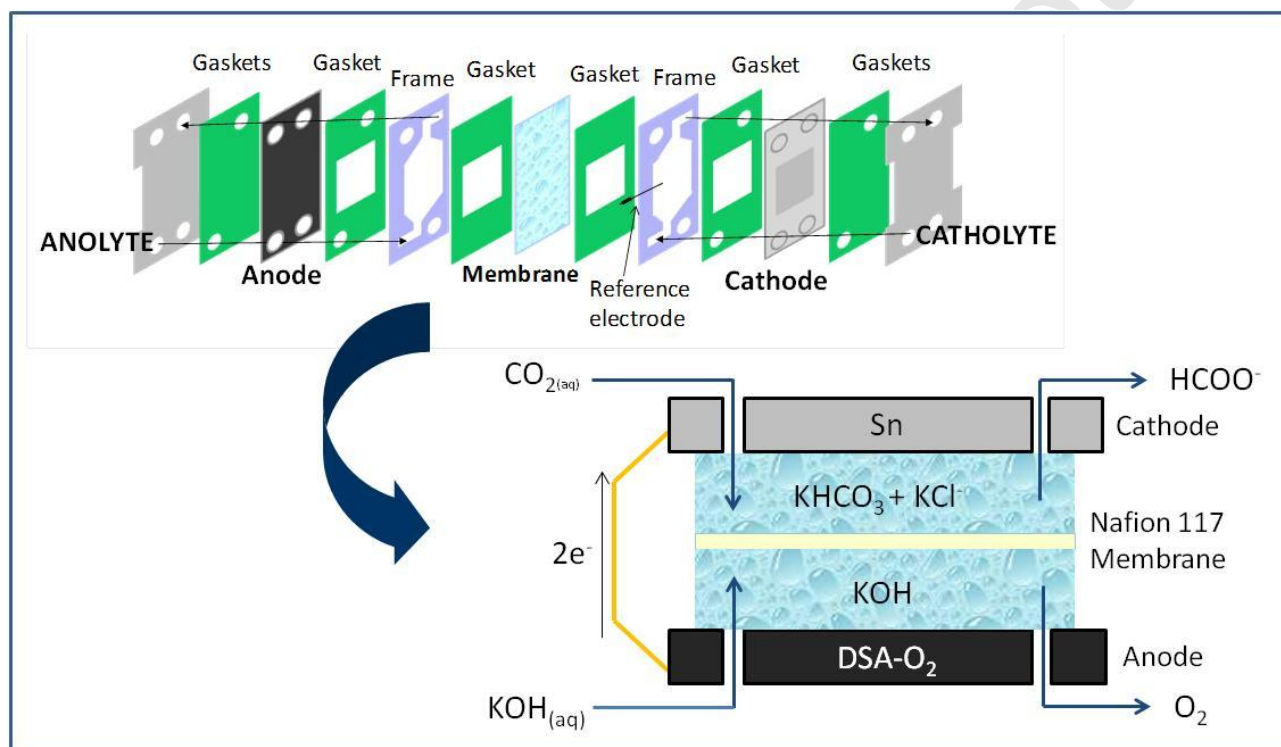
Highlights

"**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
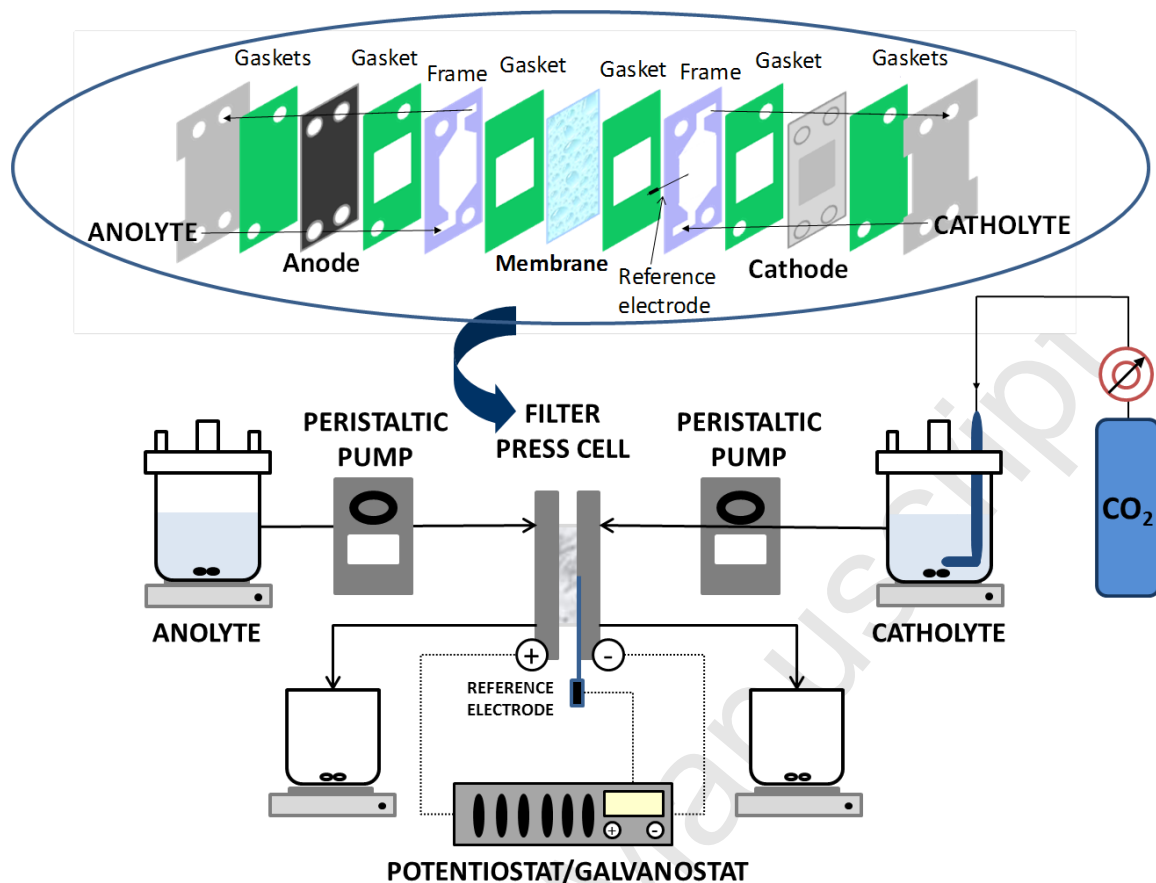
Figure 1. Diagram of the experimental set-up

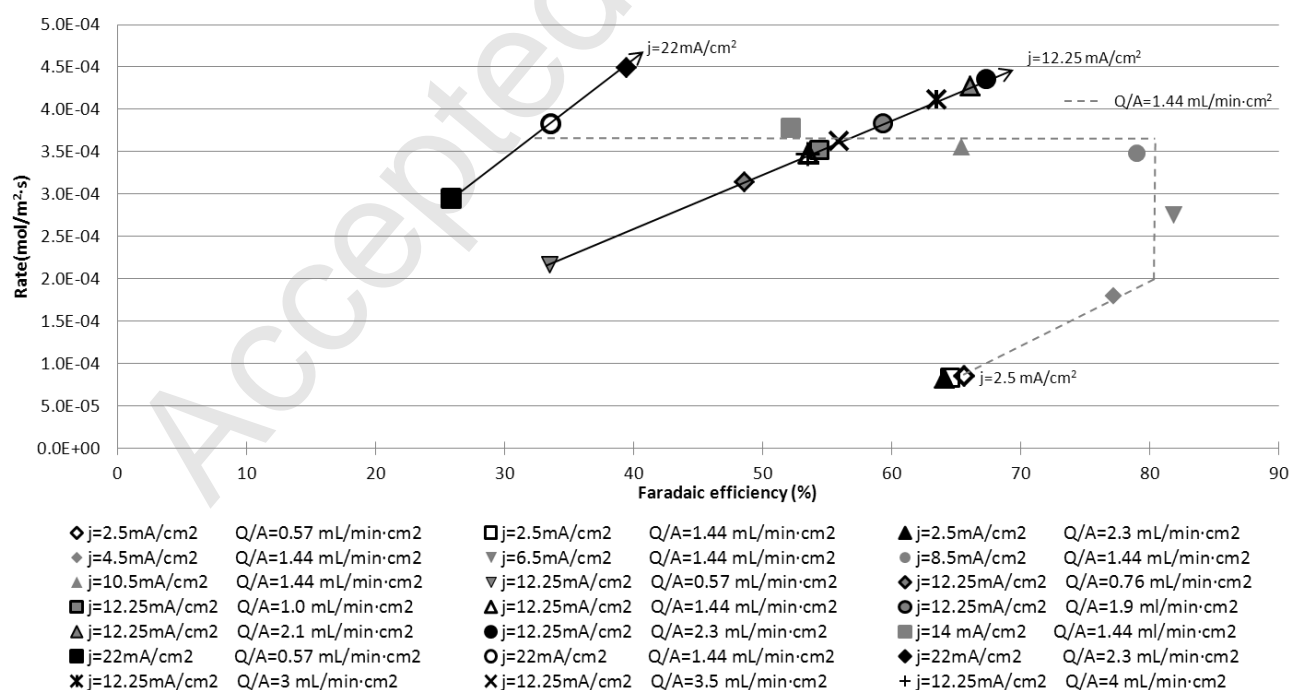|		
◇ j=2.5mA/cm2 Q/A=0.57 mL/min·cm2	□ j=2.5mA/cm2 Q/A=1.44 mL/min·cm2	▲ j=2.5mA/cm2 Q/A=2.3 mL/min·cm2
◆ j=4.5mA/cm2 Q/A=1.44 mL/min·cm2	▼ j=6.5mA/cm2 Q/A=1.44 mL/min·cm2	● j=8.5mA/cm2 Q/A=1.44 mL/min·cm2
▲ j=10.5mA/cm2 Q/A=1.44 mL/min·cm2	▽ j=12.25mA/cm2 Q/A=0.57 mL/min·cm2	◇ j=12.25mA/cm2 Q/A=0.76 mL/min·cm2
▣ j=12.25mA/cm2 Q/A=1.0 mL/min·cm2	△ j=12.25mA/cm2 Q/A=1.44 mL/min·cm2	◉ j=12.25mA/cm2 Q/A=1.9 ml/min·cm2
▲ j=12.25mA/cm2 Q/A=2.1 mL/min·cm2	● j=12.25mA/cm2 Q/A=2.3 mL/min·cm2	▣ j=14 mA/cm2 Q/A=1.44 ml/min·cm2
■ j=22mA/cm2 Q/A=0.57 mL/min·cm2	O j=22mA/cm2 Q/A=1.44 mL/min·cm2	◆ j=22mA/cm2 Q/A=2.3 mL/min·cm2
✕ j=12.25mA/cm2 Q/A=3 mL/min·cm2	✕ j=12.25mA/cm2 Q/A=3.5 mL/min·cm2	+ j=12.25mA/cm2 Q/A=4 mL/min·cm2

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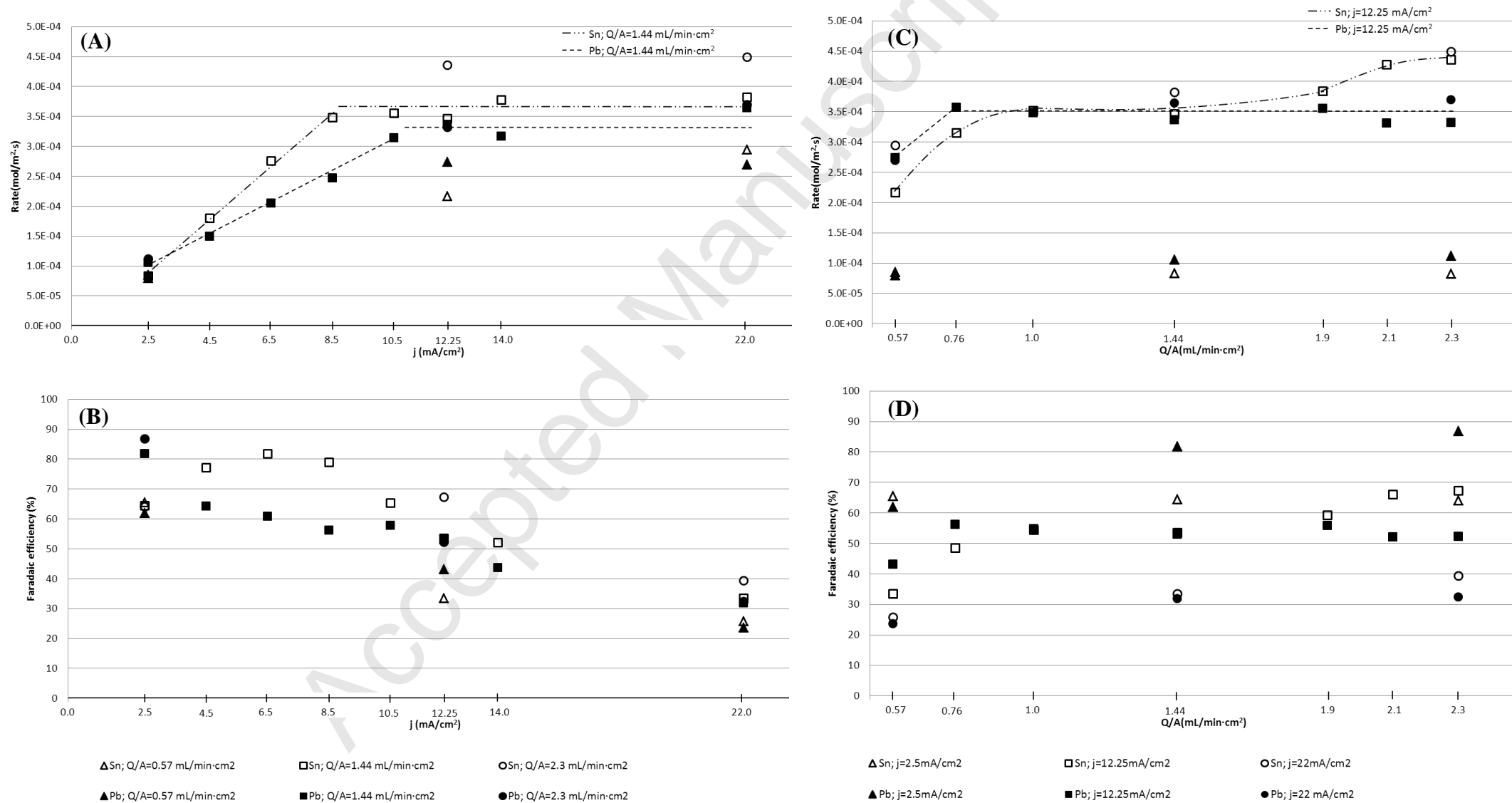
Figure 3. Comparison of the results obtained with Sn plate cathode and Pb plate cathode. (A) and (B): rates of formate production (A) and Faradaic efficiencies (B) vs current density (*j*). (C) and (D): rates of formate production (C) and Faradaic efficiencies (D) vs flow/area ratio (*Q/A*).