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ORIGINAL PAPER

Electro-reduction of carbon dioxide to formate on lead electrode in aqueous medium

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Abstract The electrochemical reduction of carbon dioxide on a lead electrode was studied in aqueous medium. Preliminary investigations carried out by cyclic voltammetry were used to determine the optimized conditions of electrolysis. They revealed that the CO_2 reduction process was enhanced at a pH value of 8.6 for the cathodic solution i.e. when the predominant form of CO_2 was hydrogenocarbonate ion. Long-term electrolysis was carried out using both potentiometry and amperometry methods in a filter-press cell in which the two compartments were separated by a cation-exchange membrane (Nafion® 423). Formate was detected and quantified by chromatography as the exclusive organic compound produced with a high Faradaic yield (from 65% to 90%). This study also revealed that the operating temperature played a key role in the hydrogenation reaction of carbon dioxide into formate in aqueous medium.

Keywords Pb electrode · CO_2 · Formate · Electro-reduction · Aqueous medium

1 Introduction

Carbon dioxide is now known to be a major cause of global warming and the technology used for its capture and storage is of great interest for researchers. However, its widespread availability can also contribute as a valuable reactant for synthesizing chemicals [1–9]. Today, there is a growing demand for formic acid which is used in pharmaceutical syntheses, as well as paper and pulp production. Moreover, a large number of papers deal with the electro-oxidation of formic acid to CO_2 [10–13]. From this viewpoint, the use of CO_2 as an infinite carbon source for producing formic acid could have specific and attractive advantages in energy conversion systems for low-power fuel cells. Metals such as Cu, Pb and Zn have been extensively studied in the electrochemical reduction of CO_2. Depending on the metal used as a cathode, the final reaction products vary considerably. This wide range of end products extends from hydrocarbons (methane, propane, ethylene…) to oxygenated molecules of which the most important are methanol, ethanol, carbon monoxide and formic and oxalic acids. The synthesis of hydrocarbons on Cu electrodes is a complex multistep reaction with adsorbed intermediates, and most notably adsorbed CO. This reaction product distribution is very sensitive to various parameters such as applied potential, buffer strength and local pH, local CO_2 concentration, CO_2 pressure and the surface crystal structure of the electrode [5, 8, 14–24]. Elsewhere, on several transition metal electrodes (Ni, Pd, Pt…) carbon monoxide was mainly formed [25–31]. Recently, there have been many extensive studies on the electro-reduction of CO_2 in different (protic or aprotic) solvents in which the solubility of the reactant varied. For instance CO_2 solubility is known to be better in methanol than in water, particularly at low temperatures (8–15 times at 273 K) [14, 16, 24]. However, the conversion of CO_2 on Pb or Cu electrodes, even if leading to the formation of formic acid, also produces other organic molecules, decreasing the selectivity and complicating the separation of end products [9, 17, 32–37].

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Among high hydrogen overvoltage electrodes with negligible CO adsorption (Hg, Cd, Pb, Tl, In and Sn) to reduce selectively CO_2 to formate in aqueous medium, lead appears to be the most straightforward and suitable cathode material for an industrial application [7, 34]. There is some controversy in the reduction about the nature of reacting species. Numerous reports in the literature have established that only dissolved CO_2 took part in the reduction, and not HCO_3^- or CO_3^{2-} ions from the solution [33, 38–44]. Meanwhile other studies have investigated this reaction in different solutions and found that the reduction was influenced by the presence of HCO_3^- [45]. Nevertheless, except the last work conducted by catalytic hydrogenation, the experimental results have indicated that the main reaction products were formic acid, hydrogen and in a small amount carbon monoxide. The present work is mainly focused on the synthesis of formate in alkaline medium on a Pb electrode. Analysis of the reaction products by chromatography was achieved during the variation of the main parameters making it possible to increase the Faradaic yield of this hydrogenation reaction.

2 Experimental

2.1 Filter press electrochemical cell

All the electrolyses were carried out at 21 ± 1 °C in a filter-press type cell, model AB (ElectroCell Systems), which contained two compartments separated by a cation exchange membrane (Nafion® 423) (Fig. 1). The working electrode (a plate of Pb 99.9% from Alfa Aesar) had a geometric surface area of 20 cm^2, while the counter electrode was a Dimensionally Stable Anode (DSA) plate. This Pt-based anode which was deposited on a titanium plate was synthesized by thermal decomposition of a polymeric precursor (DPP) as described elsewhere [46, 47]. The lead cathode was pretreated in a nitric solution (HNO_3, 25%) at room temperature and then polished. The electrode was ground flat with fine emery paper, then polished with successively finer grades of alumina powders ranging from 9.5 μm for each new electrode to 0.3 μm and rinsed with ultra-pure water by ultrasonication.

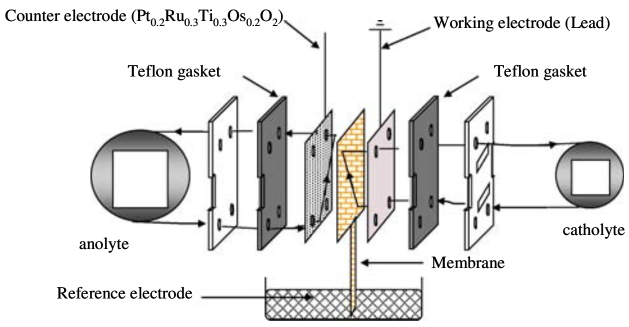

Fig. 1 Scheme of the filter press cell used to perform the electrochemical measurements

The electrolytes (100 cm^3 in each reservoir) were circulated through their own compartment using a Masterflex peristaltic pump with a flow rate of 9 mL min^{-1}. The anolyte was a 0.5 mol L^{-1} sulphuric acidic solution (pro analysis grade—Merck) because, (i) the oxidation of the solvent provided protons for the membrane to maintain its conductivity, (ii) the yield of CO_2 reduction decreased when the anolyte was an alkaline solution. In the second compartment the catholyte comprised an aqueous solution of sodium hydroxide (0.5 mol L^{-1} NaOH) in which CO_2 was dissolved at a flow rate of 150 mL min^{-1}. The bubbling was stopped when the pH value of the solution reached 8.5. Subsequently, the initial concentration of the predominant species calculated from equilibrium constants is 4.86×10^{-1} mol L^{-1} for HCO_3^- while those of the carbonate ions and CO_2 are 7.18×10^{-3} and 4.13×10^{-3} mol L^{-1}, respectively. As can be seen in Fig. 1, the control of the electrode potential was performed with part of the exchange membrane and the reference electrode ($Hg/Hg_2Cl_2/Cl^-$ (SCE)) which were ionically connected by immersing them in a saturated solution of potassium chloride.

2.2 Three-electrode conventional cell

In order to characterize the state of the electrode surface and the electrochemical behavior of the reactant, voltammetric experiments were carried out in an undivided conventional three electrodes Pyrex cell ($V = 15$ cm^3) at 21 ± 1 °C. The working electrode consisted of a lead wire with a geometric surface area of 0.42 cm^2. The current densities were normalized with the geometric surface area. A plate of vitreous carbon and $Hg/Hg_2Cl_2/KCl_{sat.}$ (SCE) served as counter and reference electrodes, respectively. This SCE electrode was separated from the solution by a Luggin-Haber capillary tip.

Electrochemical measurements were performed with a PC controlled AutoLab PGSTAT 302 Electrochemical Interface. During electrolyses, samples of the solution were taken at given times and analyzed by High Performance Liquid Chromatography (Dionex P680). This equipment comprised an Automated Sample Injector (ASI-100), an isocratic pump, a UV Detector (UVD170U) set at 210 nm, and a refractive index detector (IOTA 2). An Aminex HPX-87H column from Bio-Rad was used and the eluent was a 1 mmol L^{-1} H_2SO_4 solution at a 0.6 cm^3 min^{-1} flow rate. Acquisition of experimental data (chromatograms) was performed by a microcomputer equipped with a software package (Chromeleon) developed by Dionex.

Supporting electrolytes were prepared with ultra-pure water (18.2 MΩ cm at 273 K, MilliQ Millipore system). Suprapur NaOH and carbon dioxide gas (99.5%) were purchased from Merck and Air Liquide, respectively.

3 Results and discussion

3.1 Eelectrochemical behavior of carbon dioxide in alkaline medium

Figure 2 shows the voltammograms at a lead electrode recorded in basic medium. The first curve was measured in the presence of 0.1 mol L^{-1} K_2CO_3. It can be observed that the current densities are low when the pH value of the solution is of 12. According to the E-pH diagram performed by Hori and Suzuki [48], the predominant species at this pH are the carbonate ions, which means that this compound is not reactive at the electrode surface. As evidence, the current densities increase with the decrease of pH, i.e. when the HCO_3^- ions become more and more predominant in solution. At pH = 8.5 the bubbling of CO_2 in the cell is stopped and the equilibrium states between CO_{2aq}, HCO_3^- and CO_3^{2-} can be given as follows [48–50]: on the dissolution of gaseous carbon dioxide in water, a rapid equilibrium occurs

$$CO_{2(g)} \rightleftarrows CO_{2(aq)} \tag{1}$$

in basic solutions, Eq. 2 is written as:

$$CO_{2(aq)} + HO^- \rightleftarrows HCO_3^- \quad K_1 = 2.57 \times 10^{11} \tag{2}$$

Followed by:

$$HCO_3^- + HO^- \rightleftarrows CO_3^{2-} \quad K_2 = 8.13 \times 10^3 \tag{3}$$

The acidobasic reactions for HCO_3^- formation are accompanied by the consumption of hydroxyl and carbonate ions, confirming the decrease of the pH value in the bulk solution. The increase in the current densities in Fig. 2 (third curve) confirms the results in the literature that reported that the reduction of CO_2 would effectively occur at a pH between 7 and 9 i.e. the domain of pH where HCO_3^- is the predominant species [48, 50, 51].

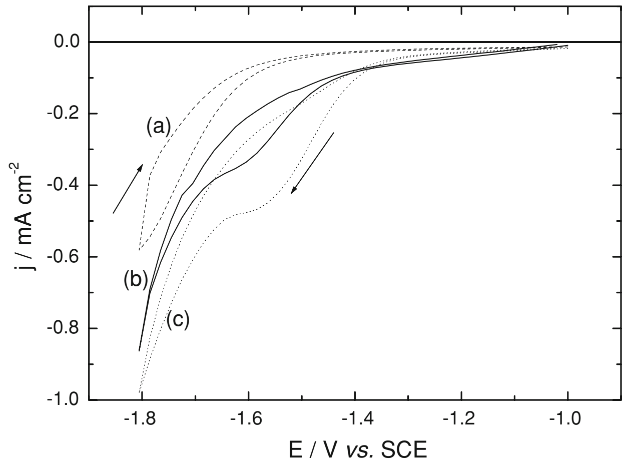

Fig. 2 Voltammograms at a Pb electrode recorded at 50 mV s^{-1} in 0.5 mol L^{-1} NaOH. (a) In presence of CO_3^{2-} (pH = 12). (b) After bubbling CO_2 (pH = 10). (c) After bubbling CO_2 (pH = 8.5)

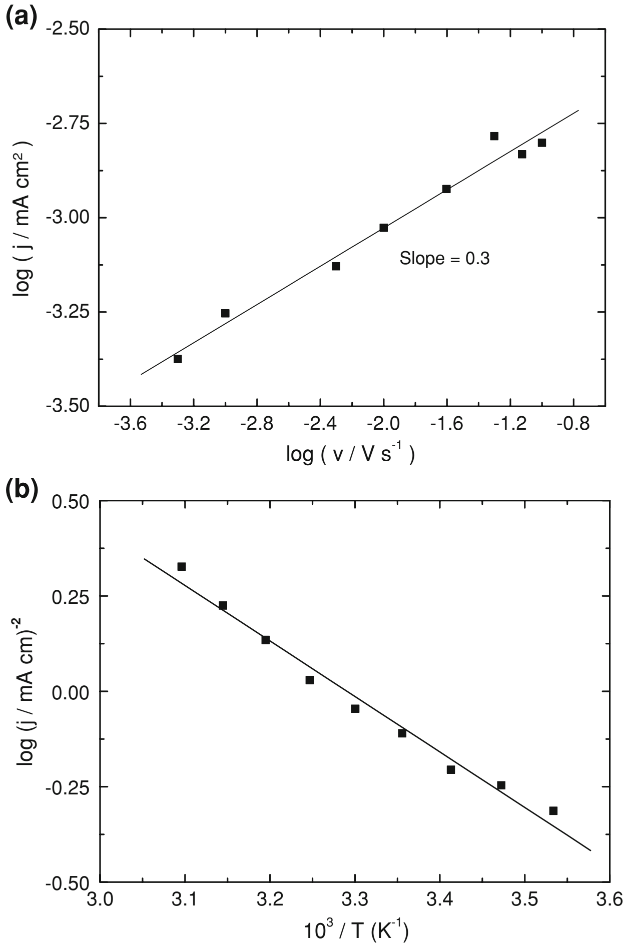

Fig. 3 Plots of log(*j*) versus log(*v*) (**a**) and versus T^{-1} (**b**) for electro-reduction of CO_2-saturated in alkaline solution (0.1 mol L^{-1} NaOH) on a Pb electrode

In order to identify the rate-determining step of CO_2 electro-reduction, CV experiments were performed at various potential sweep rates. Figure 3a represents the dependence of log(*j*) on log(*v*): *j* is the peak current density (corrected from the electrolyte contribution) expressed in mA cm^{-2} and measured at the peak potential $E_P = -1.6$ V versus SCE; *v* is the potential sweep rate, which varied from 0.5 to 100 mV s^{-1}. In terms of kinetics the mechanism is not pure from, as the slope deviates appreciably from the limiting theoretical value of either 1 (for a pure adsorption

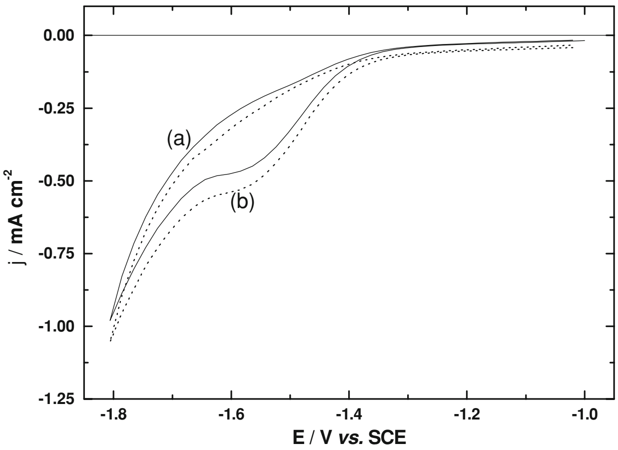

Fig. 4 Voltammograms at a lead electrode recorded in 1 mol L^{-1} NaOH after bubbling CO_2 until pH = 8.5 with a scan rate of 50 mV s^{-1}; without (a) and with (b) magnetical stirring

process) or 0.5 (for a pure diffusion process) [52–54]. As a result, the slope value of the log(*j*) versus log(*v*) straight line suggests complicated kinetics involving parallel or successive reactions.

To gain more insight into the reaction mechanism of CO_2 reduction, the effect of temperature was also studied from 5 to 40 °C under steady-state conditions, for which cyclic voltammograms were recorded at 10 mV s^{-1} (Fig. 3b). The increase in temperature involved an enhancement of current densities. The corresponding activation energy (ΔH^*) is estimated by using the following equation:

$$\left[\frac{\partial \log j_P}{\partial(1/T)}\right]_{E_{P,c}} = \frac{-\Delta H^*}{2.3R}$$

where j_P is the peak current density measured at the peak potential ($E_P = -1.6$ V versus SCE); R is the universal gas constant. The value of 28 kJ mol^{-1} (i.e. lower than 50 kJ mol^{-1}) is typical of a diffusion process [54]. Moreover, two voltammograms were recorded with and without magnetically stirring the electrolytic solution in order to support the previous statement. As can be observed in Fig. 4, the non superimposition of the $j - E$ polarization curves is probably caused by a mass transfer control.

3.2 Electrolysis of carbon dioxide on lead electrode in filter-press cell

Experimental results obtained from CO_2 reduction on a lead electrode in filter-press cell are presented in Fig. 5. The operating conditions consisted of bubbling $CO_{2(g)}$ (150 mL min^{-1}) in the catholyte (0.5 mol L^{-1} NaOH) and stopping the bubbling when the pH value reached 8.5, as previously mentioned. First electrolyses were carried out by amperometry experiments. Different electrode potentials (Fig. 5) were chosen according to Fig. 2 in the region where CO_2 reduction occurs. When applying −1.5 V versus SCE, the maximum yield reaches only 20% at 2 h. Otherwise, at −1.7 V i.e. in the hydrogen evolution reaction region, the Faradaic yield due to formate conversion decrease to a very low value. Conversely, the suitable potential value for reducing the substrate seems to be −1.6 V versus SCE in accordance with the voltammogram in Fig. 2. A maximum Faradaic yield (65%) was reached after 2 h and the pH value was close to 7.

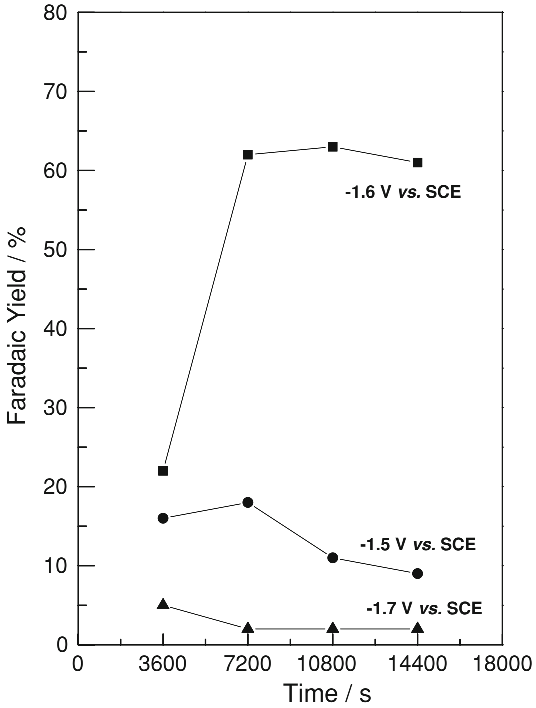

Fig. 5 Effect of cathode potential on the Faradaic yield of the formate formation on a Pb electrode in 0.5 mol L^{-1} NaOH after bubbling CO_2 until pH = 8.5

During the reaction formate was analyzed by chromatography as the exclusive organic compound produced. Although Pb is an overvoltage electrode material, the hydrogen production competes with that of formate. Taking into account the results of electrolysis at around pH = 8.5, the two following equations can be written:

At the cathode: either the reduction of hydrogenocarbonate occurs, and then it comes

$$HCO_3^- + H_2O + 2e^- \rightarrow HCOO^- + 2HO^- \qquad (4)$$

or the side reaction of water reduction occurs:

$$2H_2O + 2e^- \rightarrow H_2 + 2HO^- \qquad (5)$$

It can be noted that these reductions produce hydroxyl ions in the solution. Elsewhere, in the anodic compartment the main reaction can be written:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \qquad (6)$$

As the exchange membrane which separates the two compartments is cationic, there is no doubt that proton ions cross over it, counterbalancing ion charges and neutralizing the catholyte.

This anodic reaction is the same whatever the cathodic reaction. Resulting from Eqs. 4–6, two different global reactions can be written:

$$HCO_3{}^- \rightarrow HCOO^- + \frac{1}{2}O_2 \qquad (7)$$

and

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad (8)$$

The competition between the two reactions is directly revealed by the Faradaic yield in formate.

This implies that the $HCO_3{}^-$ reduction reaction to formate may be conducted without decreasing the pH, since the latter only decreases up to 7, which could be explained by a slight crossover of the anolyte into the catholyte.

Figure 6 shows the variation of the Faradaic yield toward formate formation with the effect of the applied current density. All the electrolysis experiments were repeatedly carried out and each Faradaic yield point is the average of three measurements. If the cathode potential remains almost stable (as its value in brackets shows), the best current density is -2.5 mA cm^{-2} with a Faradaic yield of 70% and the optimized time is 2 h.

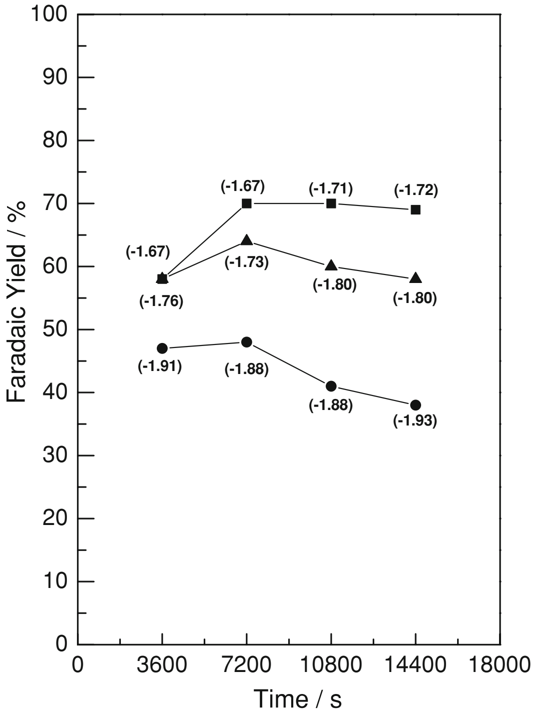

Fig. 6 Effect of current density on the Faradaic yield for formate formation on a Pb electrode in 0.5 mol L^{-1} NaOH after bubbling CO_2 until pH = 8.5 (■: -2.5 mA cm^{-2}; ▲: -5 mA cm^{-2}; ●: -10 mA cm^{-2})

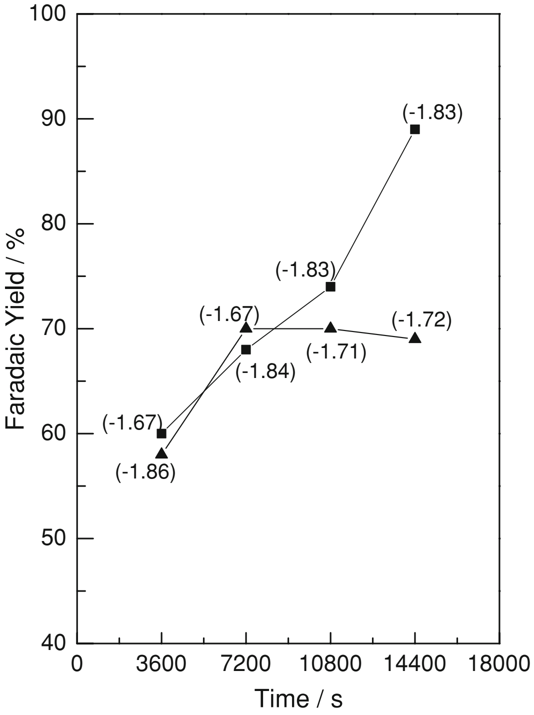

Fig. 7 Effect of operating temperature on the Faradaic yield for formate formation on a Pb electrode at -2.5 mA cm^{-2} and in 0.5 mol L^{-1} NaOH after bubbling CO_2 until pH = 8.5 (■: 4 °C; ▲: 20 °C)

Temperature is a key factor in the reduction of CO_2 by its influence on solubility. Additional electrolysis experiments were thus carried out by varying the temperature of the reservoir of the catholyte (Fig. 7) with a current density set at -2.5 mA cm^{-2}. Although the potential shifts toward HER at 4 °C, it remains stable and the production of formate increases up to a Faradaic yield of 90%. This can be explained by the fact that the low temperature slows down the hydrogen evolution reaction and favours CO_2 solubility and its mass transfer toward the cathode, which enhances formate synthesis.

As evidence, during the reaction the whole pH value remains almost constant on account of the buffer effect in the cathodic compartment.

4 Conclusion

The electro-reduction of carbon dioxide in aqueous medium was studied on a lead plate in a filter-press cell. The overall kinetics of CO_2 electro-reduction on a Pb electrode initially investigated by cyclic volammetry converged on an electrode process that was mostly controlled by diffusion. Moreover, CO_2 dissolved in the alkaline solution ($0.5\ \mathrm{mol\ L^{-1}}$ NaOH) under the operating conditions, decreased the pH value at 8.5, where predominant species are hydrogenocarbonate ions. Although H_2 production competes with dissolved CO_2 electro-reduction, $HCOO^-$ was chromatographied as the exclusive organic compound of long-term electrolysis. The competition between the reduction of CO_2 and the reduction of water and thus the Faradaic yield of formate strongly depends on the pH and on the electrode potential. Optimal results have been obtained in the 7–9 pH range and at a 1.6 V versus SCE cathodic voltage. Otherwise, the temperature of the electrolyte also has a great effect on the selectivity toward formate production which increases up to 90% when this parameter decreases from 20 to 4 °C.

References

1. Hori Y, Murata A (1990) Electrochim Acta 35:1777
2. Azuma M, Hashimoto K, Hiramoto M, Watanabe M, Sakata T (1990) J Electrochem Soc 137:1772
3. Kyriacou GZ, Anagnostopoulos AK (1993) J Appl Electrochem 23:483
4. Hara K, Tsuneto A, Kudo A, Sakata T (1994) J Electrochem Soc 141:2097
5. Jitaru M, Lowy DA, Toma M, Toma BC, Oniciu L (1997) J Appl Electrochem 27:875
6. Chaplin RPS, Wragg AA (2003) J Appl Electrochem 33:1107
7. Qu J, Zhang X, Wang Y, Xie C (2005) Electrochim Acta 50:3576
8. Gattrell M, Gupta N, Co A (2006) J Electroanal Chem 594:1
9. Subramanian K, Asokan K, Jeevarathinam D, Chandrasekaran M (2007) J Appl Electrochem 37:255
10. Rice C, Ha S, Masel RI, Wieckowski A (2003) J Power Sources 115:229
11. Lovic JD, Tripkovic AV, Gojkovic SL, Popovic KD, Tripkovic DV, Olszewski P, Kowal A (2005) J Electroanal Chem 581:294
12. Song C, Khanfar M, Pickup PG (2006) J Appl Electrochem 36:339
13. Choi J-H, Jeong K-J, Dong Y, Han J, Lim T-H, Lee J-S, Sung Y-E (2006) J Power Sources 163:71
14. Kaneco S, Iiba K, Ohta K, Mizuno T, Saji A (1998) J Electroanal Chem 441:215
15. Mizuno T, Kawamoto M, Kaneco S, Ohta K (1998) Electrochim Acta 43:899
16. Kaneco S, Iiba K, Ohta K, Mizuno T, Suzuki T (1998) Electrochim Acta 44:4701
17. Kaneco S, Iiba K, Ohta K, Mizuno T (2000) Energy Sources 22:127
18. Aydin R, Koleli F (2002) J Electroanal Chem 535:107
19. Li H, Oloman C (2005) J Appl Electrochem 35:955
20. Hara K, Tsuneto A, Kudo A, Sakata T (1997) J Electroanal Chem 434:239
21. Kaneco S, Katsumata H, Suzuki T, Ohta K (2006) Electrochim Acta 51:3316
22. Gupta N, Gattrell M, Macdougall B (2006) J Appl Electrochem 36:161
23. Taguchi S, Aramata A (1994) Electrochim Acta 39:2533
24. Hori Y, Konishi H, Futamura T, Murata A, Koga O, Sakurai H, Oguma K (2005) Electrochim Acta 50:5354
25. Hori Y, Wakebe H, Tsukamoto T, Koga O (1994) Electrochim Acta 39:1833
26. Yoshitake H, Kikkawa T, Muto G, Ota K-I (1995) J Electroanal Chem 396:491
27. Terunuma Y, Saitoh A, Momose Y (1997) J Electroanal Chem 434:69
28. Hara K, Kudo A, Sakata T (1997) J Electroanal Chem 421:1
29. Hara K, Sakata T (1997) J Electrochem Soc 144:539
30. Koleli F, Ropke T, Hamann CH (2003) Electrochim Acta 48:1595
31. Hori Y, Ito H, Okano K, Nagasu K, Sato S (2003) Electrochim Acta 48:2651
32. Kobayashi T, Takahashi H (2004) Energy Fuels 18:285
33. Udupa KS, Subramanian GS, Udupa HVK (1971) Electrochim Acta 16:1593
34. Koleli F, Atilan T, Palamut N, Gizir AM, Aydin R, Hamann CH (2003) J Appl Electrochem 33:447
35. Koleli F, Balun D (2004) Appl Catal A: General 274:237
36. Akahori Y, Iwanaga N, Kato Y, Hamamoto O, Ishii M (2004) Electrochemistry 72:266
37. Kaneco S, Iiba K, Katsumata H, Suzuki T, Ohta K (2006) Electrochim Acta 51:4880
38. Van Rysselberghe P, Alkire GJ, McGee JM (1946) J Am Chem Soc 68:2050
39. Teeter TE, Van Rysselberghe P (1954) J Chem Phys 22:759
40. Hori Y, Suzuki S (1983) J Electrochem Soc 130:2387
41. Stalder CJ, Chao S, Wrighton MS (1984) J Am Chem Soc 106:3673
42. Spichiger-Ulmann M, Augustynski J (1985) J Chem Soc Faraday Trans 81:713
43. Hori Y, Murata A, Takahashi R, Suzuki S (1987) J Chem Soc Chem Commun 728
44. Eggins BR, Bennett EM, McMullan EA (1996) J Electroanal Chem 408:165
45. Marwood M, Doepper R, Renken A (1997) Appl Catal A Gen 151:223
46. Pechini MP, Adams N (1967) US Patent 3, 330, 697:1
47. Forti JC, Olivi P, de Andrade AR (2001) Electrochim Acta 47:913
48. Hori Y, Suzuki S (1982) Bull Chem Soc Jpn 55:660
49. Sullivan BP, Krist K, Guard HE (eds) (1993) Electrochemical and electrocatalytic reactions of carbon dioxide. Elsevier, Amsterdam, p 6
50. Hori Y, Koga O, Yamazaki H, Matsuo T (1995) Electrochim Acta 40:2617
51. Li H, Oloman C (2007) J Appl Electrochem 37:1107
52. Bard AJ, Faulkner LR (1980) Electrochemical methods: fundamentals and applications. Wiley, New York
53. Beden B, Léger J-M, Lamy C (1992) Electrocatalytic oxidation of oxygenated aliphatic organic compounds at noble metal electrodes. In: Bockris JO'M et al (eds) Modern aspects of electrochemistry, vol 22. Plenum Press, New York, p 105
54. Parpot P, Kokoh KB, Beden B, Lamy C (1993) Electrochim Acta 38:1679