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CONVERSION OF CARBON DIOXIDE BY ELECTROCHEMICAL REDUCTION TO COMPOUNDS USEFUL IN FUEL CELLS

PhD Thesis Summary

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1. CARBON DIOXIDE POLLUTION

Part II

PERSONAL CONTRIBUTIONS

Key words: the electrochemical reduction of CO_2, copper electrode, lead electrode, ionic liquids, electrosynthesis.

Abbreviations:

ERCD	Electrochemical Reduction of Carbon Dioxide
HER	Hydrogen evolution reaction
IL	Ionic Liquids
FC	Fuel Cells
MAFC	Methanol- Air Fuel Cells
FAAFC	Formic Acid- Air Fuel Cells
ER	Electrochemical Reactor
CV	Cyclic Voltammetry
QCM	Quartz Crystal Microbalance
EC	Electrochemical conversion
OER	Oxygen evolution reaction

The page numbers in the contents, of figures, of equations and tables correspond to the thesis. In addition, the summary contains the entire bibliography of the thesis.

Part I

THEORETICAL ASPECTS

The continuous development of modern society characterized by the intensification of industrial activities has resulted in the pollution of the atmosphere. Carbon dioxide (CO_2) is considered to be the major cause of climate change because of its greenhouse effect and its further accumulation in the atmosphere. The atmospheric concentration of CO_2 has increased from 278 ppm during the pre-industrial period to a current level of more than 395 ppm (397.23 ppm July 2013) [1, 2].

Efforts to capture the CO_2 and to convert it into valuable chemical compounds are of great importance [4,5]. Therefore it is necessary to develop technologies for storage and / or recycling of the gas.

The electrochemical reduction of CO_2 is attractive both in theory and practice. The interest for the electrochemical reduction of CO_2 is shown by the number of papers published recently [5, 6, 11-15]. This method is a promising and efficient one, minimizing and converting CO_2 to valuable products.

The electrochemical reduction of carbon dioxide (ERCD) has several important advantages:

- Compatibility with the environment;
- Versatility;
- Energetic efficiency;
- Monitoring and management facilitated by automatic electric control of the process;
- Reasonable costs;
- ERCD is selective in relation to the products of reaction and depends on the cathode material used;
- The equipment required is relatively simple and the process can be done at moderate temperature and pressure;
- Renewable sources (solar, wind) of electricity can be used to achieve ERCD;
- In general, electrochemical systems have a compact design. The selectivity and yield of the products depends very much on the electrode material and on the electrolyte solution.

Depending on the electrode material used, electrodes in aqueous solutions can be classified according to the products of reduction, as follows [11, 16, 30]:

- Group metals Pb, Hg, In, Sn, Cd, TI and Bi (Group I) are characterized by a high overpotential for HER and CO negligible adsorption properties, and the main final product of CO_2 electroreduction is formic acid / formate ion ($HCOO^-$).

- Group metals Au, Ag and Zn, etc. (Group II) which are characterized by a moderate overpotential for HER and low CO adsorption properties. Therefore these metals can catalyze CO bond breaking in CO_2 and allow CO desorption off the electrode. As a result of this, carbon monoxide CO is the main product.

- Group metals Ni, Fe, Pt, Ti (Group III) known for their electrocatalytic character towards HER and which manifest adsorption properties towards CO. A peculiar behavior plays CO_2 electroreduction on copper because this metal yields CH_4 and C_2H_4 hydrocarbons in significant quantities.

In non-aqueous solutions there are three classes of metal electrodes which favor the formation of different products [11, 16, 30]:

- The electrodes of Pb, Tl, Hg lead to the formation of oxalic acid as a main product;

- The electrodes of Cu, Ag, Au, In, Zn and Sn on which are formed the carbon monoxide and carbon ions;

- The electrodes of the group VIII metals (Ni, Pd and Pt) which allow the formation of both CO and oxalic acid.

The electrochemical reduction of CO_2 in ionic liquids (IL) is an extension of CO_2 reduction in non-aqueous solvents and is a relatively new field. The advantages of using ionic liquids are the high solubility of CO_2 and a wide range of cathode potential due to the lack of species capable of generating hydrogen.

Most of the experiments for the reduction of CO_2 were carried out in IL with imidazolium as the cation. Amongst the reduction products, methanol and formic acid have the most important applicability. Methanol and formic acid are used as fuel in fuel cells [84-89].

The fuel cell (FC) unlike a battery, which is a closed system, consumes fuels (reactants) that are fed continuously - during cell operation. Advantages of FC-based energy generators include: the absence of pollution, operation without vibration or noise, having no moving parts and simple design and operation [86-93].

Methanol-air fuel cell (MAFC) and formic acid-air fuel cell (FAAFC).

This type of cells has several features that will be briefly described below. The diluted methanol is applied directly to the anode, where it is decomposed into protons, electrons and carbon dioxide according to the reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad (2.14)$$

Recent studies have shown that FAAFC perform much better than MAFC [94-97], this is due to the rapid kinetics of oxidation of formic acid [98-100]. Reactions underlying FAAFC are:

At the anode $HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$ $E^0 \sim -0.25V$ (vs NHE) (2.15)

At the cathode $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ $E^0 = 1.23V$ (vs NHE) (2.16)

Global reaction $HCOOH + 1/2O_2 \rightarrow CO_2 + H_2O$ (2.17)

Another feature of FAAFC is that they have a higher electromotive force, (open circuit voltage (OCV) ~ 1.48 V) than MAFC [101, 102].
The objective of this thesis is to study the electrochemical reduction of CO_2 in aqueous and ionic liquids and to obtain valuable reduction products that can be used as fuel.

To achieve the objective proposed in this thesis was developed fundamental and applied research aimed at the electrochemical reduction of CO_2.
The first part of the study focuses on the fundamental study of the electrochemical reduction of the copper electrode in alkaline carbonate and sodium bicarbonate using cyclic voltammetry coupled with experiments of electrode mass measuring (quartz crystal microbalance).

In continuation of the fundamental study on CO_2 reduction, were performed cyclic voltammetry experiments in ionic liquids on single crystals of Pt analyzing the catalytic activity of the electrodes.

In the applied study was examined the electrochemical reduction of CO_2 into the aqueous solution of Pb electrode by electrolysis in a filter press reactor. The experimental results obtained in the electrochemical reactor allowed the development of material balance model in ER and comparing its performance with the literature.

References

1. Mauna Loa Laboratory data, http://www.esrl.noaa.gov/gmd/ccgg/trends/
2. I. Omae, *Aspects of carbon dioxide utilization*, Catalysis Today, **2006**, 115, 33-52
3. M. Aresta, *Carbon Dioxide as Chemical Feedstock*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, **2010**
4. C. Genovese, C. Ampelli , S. Perathoner, G. Centi, *Electrocatalytic conversion of CO2 to liquid fuels using nanocarbon-based electrodes*, Journal of Energy Chemistry, **2013**, 22, 202–213
5. D.T. Whipple, P.J.A. Kenis, *Prospects of CO2 utilization via direct heterogeneous electrochemical reduction*, Journal of Physical Chemistry Letters, **2010**, 1, 3451-3458.
6. M A. Scibioh, B Viswanathan, *Electrochemical reduction of carbon dioxide: A status report*, Proc. Indian Natn. Sci. Acad., **2004**, 70, A, 3, 407-462
7. C.E. Bamberger, Paul R. Robinson, *Thermochemical splitting of water and carbon dioxide with cerium compounds*, Inorganica Chimica Acta ,**1980**, 42, 133–137
8. Gabriele Centi, Siglinda Perathoner, *Opportunities and prospects in the chemical recycling of carbon dioxide to fuels*, Catalysis Today, **2009**, 148, 191-205
9. K Kalyanasundaram and M Graetzel, *Artificial photosynthesis: biomimetic approaches to solar energy conversion and storage*, Current Opinion in Biotechnology, **2010**, 21, 298–310
10. Yang Lu, Zhong-yi Jiang, Song-wei Xu, Hong Wu, *Efficient conversion of CO2 to formic acid by formate dehydrogenase immobilized in a novel alginate–silica hybrid gel*,Catalysis Today, **2006**, 115, 263-268
11. M. Jitaru, D.A. Lowy, M. Toma, B. C. Toma, L. Oniciu, *Electrochemical reduction of carbon dioxide on flat metallic cathodes*, J. of Appl. Electrochem., **1997**, 27, 875-889
12. C. M. Sánchez-Sánchez, V. Montiel, D. A. Tryk, A. Aldaz, and A. Fujishima, *Electrochemical approaches to alleviation of the problem of carbon dioxide accumulation*, Pure Appl. Chem., **2001**, Vol. 73, No. 12, 1917–1927
13. R.P.S. Chaplin, A.A. Wragg, *Effects of process conditions and electrode material on reaction pathways for carbon dioxide electroreduction with particular reference to formate formation*, J. of Appl. Electrochem., **2003**, 33, 1107–1123

14. M. Łukaszewski, H. Siwek, A. Czerwiński, *Electrosorption of carbon dioxide on platinum group metals and alloys—a review*, J. Solid State Electrochem., **2009**, 13, 813–827.
15. M. Gattrell, N. Gupta, A. Co, *A review of the aqueous electrochemical reduction of CO2 to hydrocarbons at copper*, Journal of Electroanalytical Chemistry, **2006**, 594 1–19.
16. Y. Hori, H. Wakebe, T.,Tsukamoto, O, Koga, *Electrocatalytic process of CO selectivity in electrochemical reduction of* CO_2 *at metals electrodes in aqueous media,* Electrochimica Acta, **1994,** 39,1833-1839.
17. Chen YH, Kanan MW, *Tin oxide dependence of the CO2 reduction efficiency on tin electrodes and enhanced activity for tin/tin oxide thin-film catalysts,* J Am Chem Soc **2012**, 134, 1986-1989.
18. Agarwal AS, Zhai YM, Hill D, Sridhar N, *The electrochemical reduction of carbon dioxide to formate/formic acid: engineering and economic feasibility,* Chemsuschem **2011**, 4:1301-1310.
19. Furuya N, Yamazaki T, Shibata M, *High performance Ru–Pd catalysts for CO2 reduction at gas-diffusion electrodes*, J Electroanal Chem **1997**, 43, 139-41.
20. Hinogami R, Yotsuhashi S, Deguchi M, Zenitani Y, Hashiba H, Yamada Y: *Electrochemical reduction of carbon dioxide using a copper rubeanate metal organic framework,* ECS Electrochem Lett **2012**, 1:H17-H19
21. Le M, Ren M, Zhang Z, Sprunger PT, Kurtz RL, Flake JC, *Electrochemical reduction of CO2 to CH3OH at copper oxide surfaces,* Journal of Electrochemical Society **2011**, 158, E45-E49.
22. Barton Cole E, Lakkaraju PS, Rampulla DM, Morris AJ, Abelev E, Bocarsly AB, *Using a one-electron shuttle for the multielectron reduction of CO2 to methanol: kinetic, mechanistic, and structural insights,* Journal of American Chemical Society, **2010**, 132, 11539-11551.
23. Barton EE, Rampulla DM, Bocarsly AB, *Selective solar-driven reduction of CO2 to methanol using a catalyzed p-GaP based photoelectrochemical cell*, Journal of American Chemical Society, **2008**, 130, 6342-6344.
24. Dean, A. J. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, **1985**; Vol. 6-2, 9-4−9-107.

25. Hori, Y. *Electrochemical CO2 Reduction on Metal Electrodes. In Modern Aspects of Electrochemistry*; Springer: New York, **2008,** 89−189.
26. M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, T. Sakata, *Electrochemical Reduction of Carbon Dioxide on Various Metal Electrodes in Low -Temperature Aqueous* $KHCO_3$ *media*, *J.* Electroanal. Chem., **1990**, 137, 1772
27. H. Noda, S. Ikeda, Y. Oda, K. Imai, M. Maeda, K. Ito, *Electrochemical reduction of carbon dioxide at various metal electrodes in aqueous potassium hydrogen carbonate solution*, Bull. Chem. Soc. Jpn., **1990**, 63, 2459
28. M. Watanabe, M. Shibata, A. Kato, M. Azuma, T. Shibata, *Design of Alloy Electrocatalysts for* CO_2 *Reduction III . The Selective and Reversible Reduction of* CO_2 *on Cu Alloy Electrodes* J. Electrochem. Soc., **1991**, 138, 3382
29. A. Bandi, J. Schwarz, G. U. Maier, *Adsorption of* CO_2 *on Transition Metals and Metal Oxides*, J. Electrochem. Soc., **1993**, 140, 1006
30. S. Ikeda, T. Takagi, K. Ito, *Selective Formation of Formic Acid, Oxalic Acid and Carbon Monoxide by Electrochemical Reduction of Carbon Dioxide*, Bull. Chem. Soc. Jpn., **1987**, 60, 2517-2522
31. Y. Hori, K. Kikuchi, S. Suzuki, *Production of CO and* CH_4 *in electrochemical reduction of* CO_2 *at metal electrodes in aqueous hydrogencarbonate solution*, Chemistry letters, **1985,** pp. 1695-1698.
32. Y. Hori, A. Murata, *Electrochemical evidence of intermediate formation of adsorbed CO in cathodic reduction of* CO_2*, at a nickel electrode*, Electrochimica Acta, **1990**, 35, 1777-1780.
33. K. Watanabe, U. Nagashima, H. Hosoya, *An ab initio study of interactions of carbon monoxide and metal electrodes*, Chemical Physics Letters, **1993**, 209, 109–110.
34. K. Watanabe, U. Nagashima, H. Hosoya, *An ab initio study of adsorbed carbon monoxide on a metal electrode by cluster model*, Applied Surface Science , **1994**, 75, 121–124.
35. H. Noda, S. Ikeda, Y. Oda, K. Ito, *Potential Dependencies of the Products on Electrochemical Reduction of Carbon Dioxide at a Copper Electrode*, Chemistry Letters, **1989**, 18, 289-292.

36. Kyriacou, G.Z. , Anagnostopoulos, A.K, *Influence CO_2 partial pressure and the supporting electrolyte cation on the product distribution in CO_2 electroreduction*, Journal of Applied Electrochemistry, **1993**, 23, 483-486.
37. J. J. Kim, D. P. Summers,K. W. Frese, *Reduction of CO_2 and CO to methane on Cu foil electrodes* Journal of Electroanalytical Chemistry, **1988**, 245**,** 223-244
38. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Vol. 2, Plenum Press, New York, **1970.**
39. Y. Hori, H. Konishi,T. Futamura, *Deactivation of copper electrode in electrochemical reduction of CO2* Electrochimica Acta, **2005**, 50, 5354-5369.
40. D. W. DeWulf, Tuo Jin, Allen J. Bard, *Electrochemical and Surface Studies of carbon dioxide reduction to Methane and Ethylene at Copper Electrodes in Aqueous Solutions*, Journal of Electrochemical Society, **1989**, 136, 1686.
41. S. Wasmus, E. Cattaneo, *Reduction of carbon dioxide to methane and ethene-An on-line MS study with rotating electrodes*, Electrochimica Acta, **1990**, 35, 771-775.
42. G.Kyriacou, , A. Anagnostopoulos, *Electroreduction of CO_2 on differently prepared copper electrodes. The influence of electrode treatment on the current efficiences*, Journal of Electroanalytical Chemistry, **1992**, 322, 233-246.
43. B. Jermann, J. Augustynski, *Long-term activation of the copper cathode in the course of CO_2 reduction,* Electrochimica Acta, **1994**, 39, 1891-1896.
44. Jaeyoung Lee, Yongsug Tak, *Electrocatalytic activity of Cu electrode in electroreduction of CO_2* Electrochimica Acta, **2001**, 46, 3015-3022.
45. Y. Terunuma, A. Saitoh, Y. Momose, *Relationship between hydrocarbon production in the electrochemical reduction of CO_2 and the characteristics of the Cu electrode*, Journal of Electroanalytical Chemistry, **1997**, 434, 69-75
46. Tin-Yu Chang, Ru-Meng Liang, Pu-Wei Wu , Jing-Yu Chen, Yu-Chi Hsieh, *Electrochemical reduction of CO_2 by Cu_2O-catalyzed carbon clothes*, Materials Letters, **2009**, 63, 1001-1003
47. Karl W. Frese, Jr., *Electrochemical reduction of CO_2 at intentionally oxidized copper electrodes*, J. Electrochem. Soc., **1991**, 138, 3338-3344
48. M. Le, M. Ren,, Z. Zhang, P. T. Sprunger, R. L. Kurtz, and J. C. Flake, *Electrochemical reduction of CO_2 to CH_3OH at Copper oxide surfaces*, Journal of the electrochemical Society, **2011**, 158, 45-49

49. K. Ogura, H. Yano,F. Shirai, *Catalytic reduction of* CO_2 *to ethylene by electrolysis at a three-phase interface,* Journal of the Electrochemical Society, **2003**, 150, 163-168
50. K. Ogura, R. Oohara,Y. Kudo, *Reduction of* CO_2 *to ethylene at three-phase interface effects of electrode substrate and catalytic coating,* Journal of the Electrochemical Society, **2005**, 152**,** 213-219.
51. H. Yano, T. Tanaka, M. Nakayama,K. Ogura, *Selective electrochemical reduction of* CO_2 *to ethylene at a three-phase interface on copper(I) halide-confined Cu-mesh electrodes in acidic solutions of potassium halides,* Journal of Electroanalytical Chemistry, **2004**, 565**,** 287-290.
52. F.Koleli, T. Atilan, N. Palamut, A. M. Gizir, Journal of Applied Electrochemistry, **2003**, 33, 447-450
53. Fatih Koleli, Didem Balun, Applied Catalysis A: General, **2004**, 274, 1-2, 237-242
54. M. Todoroki, K. Hara, A. Kudo, T. Sakata, *Electrochemical reduction of high pressure* CO_2 *at Pb, Hg and In electrodes in an aqueous* $KHCO_3$ *solution*, Journal of Electroanalytical Chemistry, **1995**, 394, 199-203
55. B. R. Eggins C. Ennis R. McConnell – *Journal of Applied Electrochemistry*. **27** (1997) 706
56. B. Innocent, D. Pasquier, F. Ropital, *Applied Catalysis B: Environmental* **98** (2010) 65-71
57. S. Kaneco, R. Iwao, K. Iiba, *Energy (Oxford)* **23** (1998) 1107
58. K.Ito, S. Ikeda, N. Yamaughi, T. Iida, *Bulletin of the Chemical Society of Japan* **58**, (1985) 3027-3028
59. K.Ito, S. Ikeda, N. Yamaughi, T. Iida, *Bulletin of the Chemical Society of Japan* **60,** (1987) 2517-2522
60. C. Amatore J.-M. Saveant – *Journal of American Chemical Society* **103** (1981) 5021
61. Hori Y, Murata A, Takahashi R, *Formation of hydrocarbons in the electrochemical reduction of carbon-dioxide at a copper electrode in aqueous-solution*. J Chem. Soc Faraday Trans I **1989**, 85, 2309-2326.
62. Murata A, Hori Y, *Product selectivity affected by cationic species in electrochemical reduction of CO2 and CO at a Cu electrode,*. Bull Chem Soc Jpn **1991**, 64:123-127
63. Wu JJ, Risalvato FG, Ke FS, Pellechia PJ, Zhou XD, *Electrochemical reduction of carbon dioxide I. Effects of the electrolyte on the selectivity and activity with Sn electrode*. J Electrochem Soc **2012**, 159:F353-F359

64. Thorson MR, Siil SI, Kenis PJA, *Effect of cations on the electrochemical conversion of CO2 to CO*,. J Electrochem Soc **2013**, 160:F69-F74
65. K. Ohta, K. Kawamoto, T. Mizuno, D.A. Lowy, *Electrochemical reduction of carbon dioxide in methanol at ambiant temperature and pressure*, Journal of Applied Electrochemistry,**1998**, 28 717
66. S. Kaneco, K. Iiba, K. Ohta, T. Mizuno and A. Saji, *Electrochemical reduction of* CO_2 *on Au in KOH + methanol at low temperature*, Journal of Electroanalytical Chemistry, **1998**, 441, 215-220
67. K. Tamura, S.Miyaguchi , K. Sakaue, Y. Nishihata, J. Mizuki, *Direct observation of Au(111) electrode surface structure in bis(trifluoromethylsulfonyl)amide-based ionic liquids using surface X-ray scattering*, Electrochemistry Communications, **2011**, 13, 411–413
68. R. Atkin, N. Borisenko, M. Druschler, S. Z. El Abedin, F. Endres, R. Hayes, B. Huber and B.Roling, *An in situ STM/AFM and impedance spectroscopy study of the extremely pure 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate/Au(111) interface: potential dependent solvation layers and the herringbone reconstruction*, Phys. Chem. Chem. Phys., **2011**, 13, 6849–6857
69. Neil V. Rees, Richard G. Compton, *Electrochemical CO2 sequestration in ionic liquids; a perspective*, Energy Environ. Sci., **2011**, 4, 403–408
70. H. Ohno, *Electrochemical aspects of ionic liquids*,Wiley, **2011**, second edition
71. Husson-Borg, P.; Majer, V.; Gomes, M. F. C. *Solubilities of oxygen and carbon dioxide in butyl methyl imidazolium tetrafluoroborate as a function of temperature and at pressures close to atmospheric pressure.* J. Chem. Eng. Data **2003**, *48*, 480-485.
72. J. Blath, M. Christ, N. Deubler, T. Hirth, T. Schiestel - *Gas solubilities in room temperature ionic liquids – Correlation between RTiL-molar mass and Henry's law constant*, Chemical Engineering Journal **2011,** 172, 167– 176
73. A. Finotello, J. E. Bara, D. Camper and R. D. Noble, *Room-Temperature Ionic Liquids: Temperature Dependence of Gas Solubility Selectivity*, Ind. Eng. Chem. Res. **2008**, *47*, 3453-3459.
74. C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke, and E. J. Maginn, *Why Is* CO_2 *So Soluble in Imidazolium-Based Ionic Liquids?* J. AM. CHEM. SOC. **2004**, 126, 5300-5308

75. Y. Hou and R. E. Baltus, *Experimental Measurement of the Solubility and Diffusivity of CO2 in Room-Temperature Ionic Liquids Using a Transient Thin-Liquid-Film Method*, Ind. Eng. Chem. Res. **2007**, *46,* 8166-8175
76. S. S. Moganty and R. E. Baltus, *Regular Solution Theory for Low Pressure Carbon Dioxide Solubility in Room Temperature Ionic Liquids: Ionic Liquid Solubility Parameter from Activation Energy of Viscosity*, Ind. Eng. Chem. Res. **2010**, *49*, 5846–5853.
77. Benjamin C. M. Martindale, Richard G. Compton, *Formic acid electro-synthesis from carbon dioxide in a room temperature ionic liquid*, Chem. Commun., **2012**, 48, 6487–6489
78. G. Zhao, T. Jiang, B. Han, Z. Li, J. Zhang, Z. Liu, J.He, W. Wu - *Electrochemical reduction of supercritical carbon dioxide in ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate*, J. of Supercritical Fluids, **2004**, 32, 287–291
79. L. L. Snuffin, Louis W. Whaley, and L. Yu - *Catalytic Electrochemical Reduction of CO2 in Ionic Liquid EMIMBF3Cl*, Journal of The Electrochemical Society, **2011**, 158, 155-158
80. L. E. Barrosse-Antle and R. G. Compton - *Reduction of carbon dioxide in 1-butyl-3-methylimidazolium acetate,* Chem. Commun., **2009**, 3744–3746
81. S. Nakagawa, A. Kudo, M. Azuma, T. Sakata, *Effect of pressure on the electrochemical reduction of CO, on Group VIII metal electrodes*, J. Electroanal. Chem., **1991**, 308, 339-343
82. M. Todoroki, K. Hara, A. Kudo, T. Sakata, *Electrochemical reduction of high pressure* CO_2 *at Pb, Hg and In electrodes in an aqueous* $KHCO_3$ *solution*, Journal of Electroanalytical Chemistry, **1995**, 394, 199-203
83. S. Kaneco, N. H. Y. Xing, H. Katsumata, H. Ohnishi, T. Suzuki, K. Ohta, *Electrochemical conversion of carbon dioxide to methane in aqueous* $NaHCO_3$ *solution at less than 273 K*, Electrochimica Acta **2002**, 48, 51–55
84. Jong-Ho C., Kyoung-Jin J. , Y.Dong, J. Hanb, Tae-Hoon L., Jae-Suk Lee, Yung-Eun Sung, *Electro-oxidation of methanol and formic acid on PtRu and PtAu for direct liquid fuel cells*, Journal of Power Sources, **2006**, 163, 71–75
85. Su Ha, Cynthia A. Rice, Richard I. Masel, Andrzej Wieckowski, *Methanol conditioning for improved performance of formic acid fuel cells,* Journal of Power Sources, **2002**, 112, 655–659

86. S. Wasmus, A.Kuver, *Methanol oxidation and direct methanol fuel cells: a selective review*, Journal of Electroanalytical Chemistry **1999**,461, 14 – 31
87. R. Chetty, K. Scott, *Direct ethanol fuel cells with catalysed metal mesh anodes*, Electrochimica Acta, **2007**, 52, 4073–4081
88. A. Oedegaard, C. Hentschel, *Characterisation of a portable DMFC stack and a methanol-feeding concept, J. Power Sources*, **2006**, 158, 177-187
89. S. Uhm, S.T. Chung, J. Lee, *Activity of Pt anode catalyst modified by underpotential deposited Pb in a direct formic acid fuel cell,* Electrochem. Commun., **2007**, 9, 2027-2031
90. S.J. Kang, J. Lee, J.K. Lee, C.Y. Chung, Y. Tak, *Influence of Bi Modification of Pt Anode Catalyst in Direct Formic Acid Fuel Cells*, J. Phys. Chem. B, **2006**, 110, 7270-7274
91. R. Dillon, S. Srinivasan, A.S. Arico, V. Antonucci, *International activities in DMFC R&D: status of technologies and potential applications*, J. Power Sources, **2004**, 127, 112-126
92. C. Rice, S. Ha, R.I. Masel, A. Wieckowski, *Catalysts for direct formic acid fuel cells,* J. Power Sources, **2003**, 115, 229-235
93. S. Ha, R. Larsen, R.I. Masel, *Performance characterization of Pd/C nanocatalyst for direct formic acid fuel cells*, J. Power Sources, **2005**, 144, 28-34
94. Y.F. Zhang, P. Zhang, H. He, B. Zhang, Z.Y. Yuan, X.W. Liu, *A self-breathing metallic micro-direct methanol fuel cell with the improved cathode current collector,* Int J Hydrogen Energy, 2011, 36, 857–868
95. H.I. Joh, S.Y. Hwang, J.H. Cho, T.J. Ha, S.K. Kim, S.H. Moon, *Development and characteristics of a 400 W-class direct methanol fuel cell stack,* Int J Hydrogen Energy, **2008**, 33, 7153–7162
96. L. Feng, W. Cai, C. Li, J. Zhang, C. Liu, W. Xing, *Fabrication and performance evaluation for a novel small planar passive direct methanol fuel cell stack*, Fuel, **2012**, 94, 401–408
97. L. Feng, J. Zhang, W. Cai, Liangliang, W. Xing, C. *Liu Single passive direct methanol fuel cell supplied with pure methanol,* J Power Source, **2011**, 196, 2750–2753

98. J. Shim, J. Lee, Y. Ye, J. Hwang, S.-K. Kim, T.-H. Lim, *One-pot synthesis of intermetallic electrocatalysts in ordered, large-pore mesoporous carbon/silica toward formic acid oxidation*, ACS Nano, **2012**, 6, 6870–6881

99. X. Zhao, J. Zhu, L. Liang, C. Liu, J. Liao, W. Xing, *Enhanced electroactivity of Pd nanocrystals supported on H3PMo12O40/carbon for formic acid electrooxidation*, J Power Source, **2012**, 210, 392–396

100. S. Zhang, Y. Shao, G. Yin, Y. Lin, *Electrostatic self-assembly of a Pt-around-Au nanocomposite with high activity towards formic acid oxidation*, Angew Chem Int Ed, **2010**, 49 , 2211–2214

101. U.B. Demirci, *Direct liquid-feed fuel cells: Thermodynamic and environmental concerns J. Power Sources*, **2007**, 169, 239-246

102. C. Rice, R.I. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, *Direct formic acid fuel cells*, J. Power Sources, **2002**, 111, 83-89

103. Y. Hori, O. Koga, H. Yamazaki, T. Matsuo, *Infrared spectroscopy of adsorbed CO and intermediate species in electrochemical reduction of CO_2 to hydrocarbons on a Cu electrode*, Electrochimica Acta, **1995**, 40, 2617-2622

104. I. Oda, H. Ogasawara, M. Ito, *Carbon Monoxide Adsorption on Copper and Silver Electrodes during Carbon Dioxide Electroreduction Studied by Infrared Reflection Absorption Spectroscopy and Surface-Enhanced Raman Spectroscopy*, Langmuir, **1996**, 12, 1094–1097

105. Paik W., Andersen T. N., Eyring, H., *Kinetic studies of the electrolytic reduction of carbon dioxide on the mercury electrode*, Electrochimica Acta, **1969**, 14, 1217-1232

3. METHODS USED

Cyclic voltammetry (CV) is the most used technique to obtain qualitative information about electrochemical reactions. Cyclic voltammetry is useful for the study of electroactive species on the electrode surface. This technique allows observation in a short time of a large range of potential redox properties of these species (information on the kinetics of heterogeneous electron transfer reactions and processes information about adsorption or coupled chemical reactions)[1-5]

Electrochemical cells used in cyclic voltammetry have three electrodes: a working electrode, a reference electrode and an auxiliary electrode. Electroactive species react to the working electrode surface. The most commonly used reference electrodes are standard calomel electrode (SCE) and electrode Ag / AgCl / KClsat. A platinum wire is often used as auxiliary electrode.

Quartz crystal microbalance (QCM) is a very sensitive device capable of recording in situ adsorption on electrodes of very small amounts of species in solution [6]. Due to the high sensitivity of the QCM it can be used to study processes occurring at the interface [6-10]. The principle of the technique is to measure changes in frequency of the quartz crystal.

Electrolysis can be used not only for the purpose of decomposition of substances but also for the production of new substances in an electrochemical cell or electrochemical reactor. The formation of new substances to the electrode depends on the current which crosses the interface, and may be described quantitatively by Faraday's law [1, 2].

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References

1. A. J. Bard, L. R. Faulkner, *Electrochemical Methods-Fundamentals and Applications*, John Wiley & Sons, **2001**
2. A. Popescu, C. Tigae, *Metode electrochimice de analiza*, Reprografia universitatii din Craiova, **2000**
3. Joseph Wang, *Analytical Electrochemistry*, WILEY-VCH, **2001**
4. A. M. Bond, *Broadening Electrochemical Horizons, Principles and Illustration of Voltammetric and Related Techniques*, OXFORD UNIVERSITY PRESS, **2002**
5. D.K.Gosser(Ed) ,*Cyclic Voltammetry*,VCH,New York, **1994**
6. W. Visscher, J. F. E. Gootzen, A.P.Cox, J.A. R. van Veen, *Electrochemical quartz crystal microbalance measurements of CO adsorption and oxidation on Pt in various electrolytes*, Electrochimica Acta, **1998**, 43, 533-547.
7. J. Lee, Y. Tak, *Electrocatalytic activity of Cu electrode in electroreduction of* CO_2 Electrochim. Acta, **2001**, 46, 3015-3022.
8. V. S.J. Craig, M. Plunkett, *Determination of coupled solvent mass in quartz crystal microbalance measurements using deuterated solvents*, J. of Colloid and Interf. Science **2003**, 262, 126–129.
9. B. I. Lemon, J.T. Hupp, *Electrochemical Quartz Crystal Microbalance Studies of Electron Addition at Nanocrystalline Tin Oxide/Water and Zinc Oxide/Water Interfaces: Evidence for Band-Edge-Determining Proton Uptake*, J. Phys. Chem. B, **1997,** 101, 2426-2429.
10. F. Deng, S. Chen, *Electrochemical Quartz Crystal Microbalance Studies of the Rectified Quantized Charging of Gold Nanoparticle Multilayers*, Langmuir **2007**, *23*, 936-941.

4. CATHODIC REDUCTION OF CO_2 ON COPPER ELECTRODE-CYCLIC VOLTAMMETRY [1]

Cyclic voltammetry experiments were carried out on the copper electrode in carbonate / hydrogen carbonate solutions, in the potential domain between 0.0 and -0.7 V to several scanning speeds. The results obtained in $Na_2CO_3/NaHCO_3$, pH = 9.3, are shown in **Fig. 4.2.**

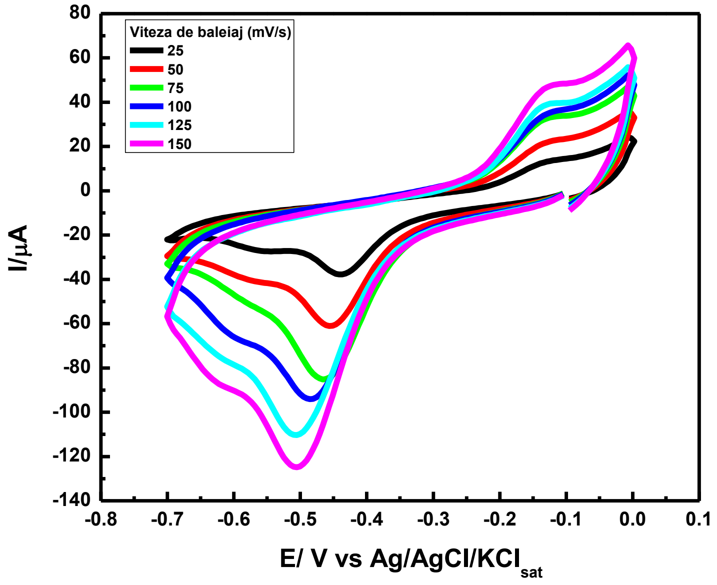


Fig. 4.2 The cyclic voltammograms on copper electrode in $Na_2CO_3/NaHCO_3$, (pH=9.3)

Voltammograms (**Fig. 4.2**) describe an irreversible process (the charge transfer is the rate limiting step), since the form seen in a reduction peak potential of -0.6V~is different form the oxidation peak appeared at~-0.2V. In the irreversible processes, the peak potential Ep (V) depends on the scanning speed. According to the literature [14], the difference between the peak potential (Epc) and the potential for semi-peak (Ep/2) has a value of 47.7/αza. We have calculated the values of α (the coefficient of charge transport) and were 0.9.

Peak currents help to identify the type of process that takes place at the electrode surface. For this we studied the effect of scan rate on the current cathodic peak Ipc.

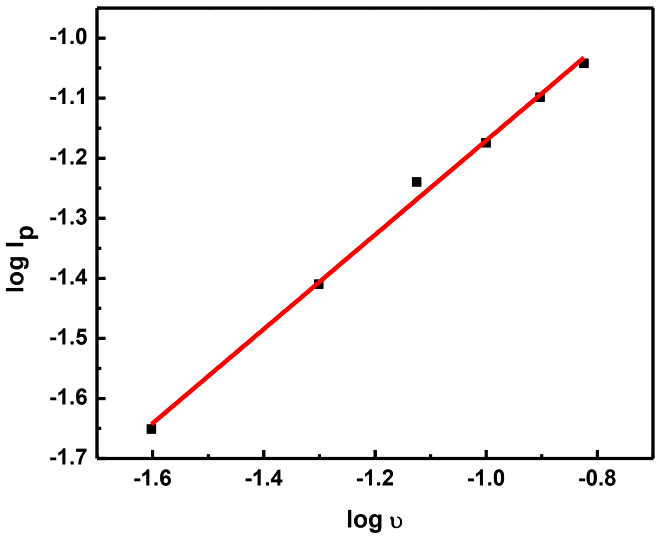


Fig. 4.3 The dependence of the logarithm of the peak current (log Ip) with logarithm of scan rate (log ν)

The dependence of the logarithm of the peak current (log Ip) with scan rate (log ν) is linear and increases with increasing scan rate in the range 25-150 mV/s. This can be seen in **Fig. 4.3**. for the solution with pH=9.3. The slope obtained is 0.77 (R2 = 0.995), this corresponds to a mixed diffusion-adsorption control [15].

The influence of $HCO_3^-$and CO_3^{2-}anions changes the pH and thus the nature and amount of product formed. Hori et al. [8] showed that the distribution of the products of the reduction of CO_2 depends on the type of electrolyte and pH.

A graphical representation of the potential of peak E_{pc} vs pH shows a shift of E_p to more negative potential values with increasing pH **Fig. 4.4**. This behavior indicates that the hydrogen ions have a strong effect on the redox behavior of the studied system, and at least one of the reactants of the process is influenced by pH.

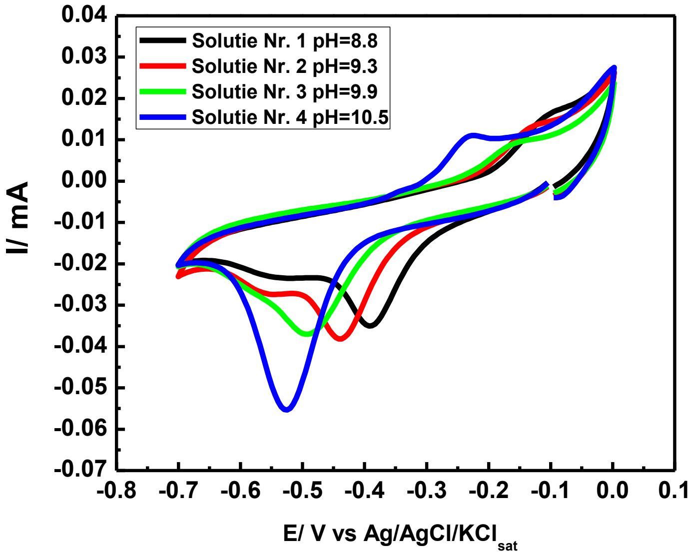


Fig.4.4 The influence of pH on the potential of the electrode at scan rate of 25 mV/s

If the I_p and scan rate linear correlation provides information about the type of process, the slope obtained by plotting the dependence E_p by scan rate ν (**Fig. 4.5**), gives information about "α" and „z_a”.

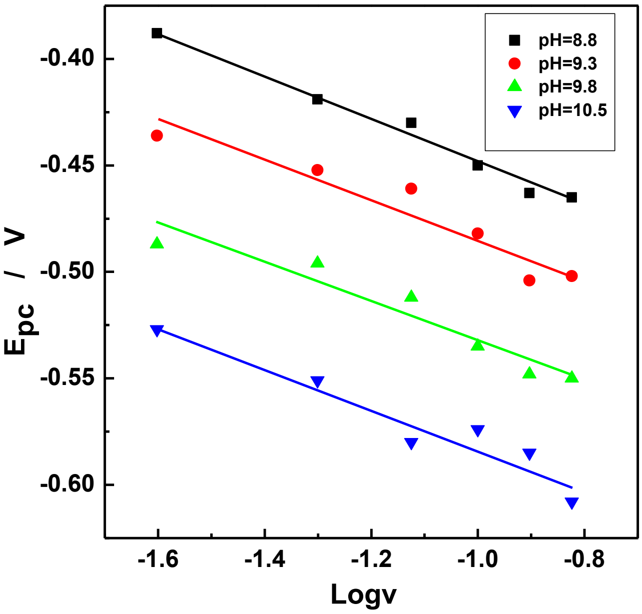


Fig. 4.5 E_{pc} dependence on the logarithm of the scan rate (log ν) at different pH values.

Table 4.3 Slopes and ordinates of the lines corresponding to the 4 electrolyte solutions

pH	**Slope, d E_p/d log v (V)**	**Ordinate, $E_p|_{v=1}$ (V)**	**R^2**	**αz_a**
8.8	- 0.102	- 0.551	0.983/7	0.290
9.3	- 0.091	- 0.576	0.891/7	0.325
9.8	- 0.090	- 0.622	0.895/7	0.331
10.5	- 0.095	- 0.677	0.908/7	0.313

The dependence of the ordonate with pH is linear (**Fig. 4.6**) and the slope was -0.076.

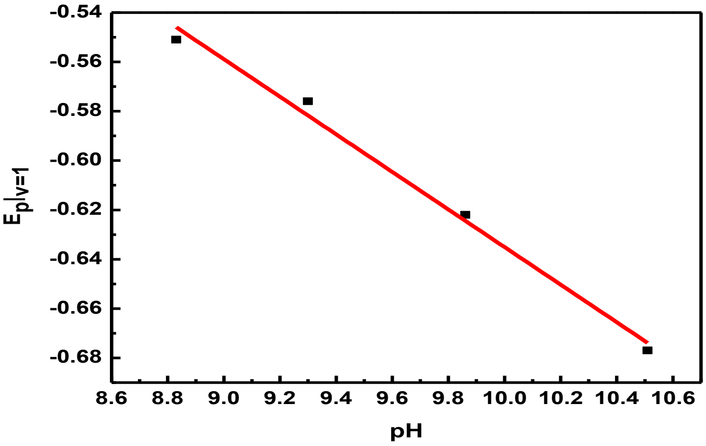


Fig. 4.6 The dependence $E_p|_{v=1}$ *vs.* pH

According with these results we suggested the transfer of an electron and a proton for the rate determining step.

References

1. F. A. Hanc, P. Ilea, *Electrochemical reduction of CO2 I. Cyclic voltammetry (CV) studies at a copper electrode*, **Poster**, „The International Conference ENVIRONMENT & PROGRESS Environment-Research, Protection and Management" , Cluj-Napoca, **2011.**
2. C. Genovese, C. Ampelli, S. Perathoner, G. Centi, *Electrocatalytic conversion of CO2 to liquid fuels using nanocarbon-based electrodes*, Journal of Energy Chemistry **2013**, 22, 202–213
3. M.R. Goncalves, A. Gomes, J. Condeco, T.R.C. Fernandes, T. Pardal,C.A.C. Sequeira, J.B. Branco, *Electrochemical conversion of CO2 to C2 hydrocarbons using different ex situ copper electrodeposits*, Electrochimica Acta, **2013**, 102, 388– 392
4. H. Jhong, S. Ma, P. JA Kenis, *Electrochemical conversion of CO2 to useful chemicals: current status, remaining challenges, and future opportunities*, Current Opinion in Chemical Engineering, **2013**, 2, 191–199
5. H.Wang, D. Y.C. Leung, J. Xuan, *Modeling of a microfluidic electrochemical cell for CO2 utilization and fuel production*, Applied Energy **2013**, 102, 1057–1062
6. P. Van Rysselberghe, G. J. Alkire, and J. M. McGee, *Polarographic reduction waves from carbon dioxide solutions*, J. Amer. Chem. Soc., **1946**, 68, 2050
7. K. S. Udupa, G. S. Subramanian, and H. V. K. Udupa, *The electrolytic reduction of carbon dioxide to formic acid*, Electrochimica Acta, **1971**, 16, 1593
8. Hori Y, Murata A, Takahashi R, *Formation of hydrocarbons in the electrochemical reduction of carbon-dioxide at a copper electrode in aqueous-solution*. J Chem. Soc Faraday Trans I **1989**, 85, 2309-2326.
9. Murata A, Hori Y, *Product selectivity affected by cationic species in electrochemical reduction of CO2 and CO at a Cu electrode,*. Bull Chem Soc Jpn **1991**, 64:123-127
10. Wu JJ, Risalvato FG, Ke FS, Pellechia PJ, Zhou XD, *Electrochemical reduction of carbon dioxide I. Effects of the electrolyte on the selectivity and activity with Sn electrode*. J Electrochem Soc **2012**, 159:F353-F359
11. Thorson MR, Siil SI, Kenis PJA, *Effect of cations on the electrochemical conversion of CO2 to CO,*. J Electrochem Soc **2013**, 160:F69-F74
12. Joseph Wang, *Analytical Electrochemistry*, WILEY-VCH, **2001**

13. A. M. Bond, *Broadening Electrochemical Horizons, Principles and Illustration of Voltammetric and Related Techniques*, OXFORD UNIVERSITY PRESS, **2002**
14. Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods-Fundamentals and Applications*, John Wiley & Sons, **2001**
15. D.K.Gosser(Ed) ,*Cyclic Voltammetry*, VCH, New York, **1994**

5. MASS MEASUREMENT OF COPPER ELECTRODE USING QUARTZ CRYSTAL MICROBALANCE [1]

The experiments with quartz crystal microbalance were coupled with cyclic voltammetry measurements. The scans use a four potential scheme, when an initial reduction scan, from -0.1 to -0.65V, is followed by an oxidation scan, to 0V, and the cycle is completed by a reduction scan to the initial -0.1V value.

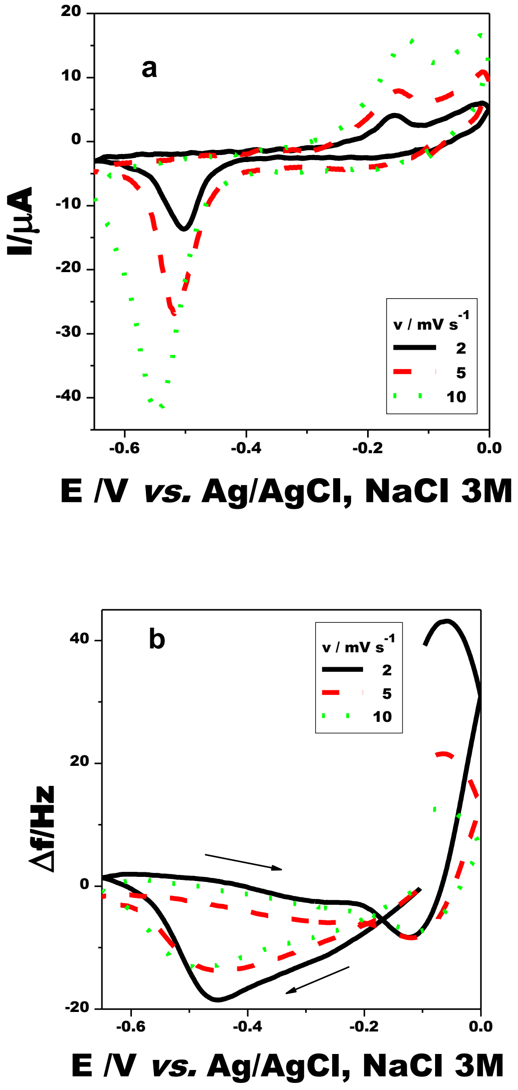


Fig. 5.2. Influence of scan rate on current intensity (a) and resonance frequency shift (b) for pH=10.51.

As can be seen in **Fig. 5.2**, for pH=10.51, the voltammograms present a single cathodic peak, at potentials between -0.5 and -0.55V, and two consecutive anodic peaks at approx. -0.15 and

-0.025V. Only the last anodic peak exhibits an approx. proportionality between the peak current and square root of the scan rate, which is an indication of the involvement of diffusion of reactants. On the contrary, for the other two peaks the slopes of Ip *vs* v plots in logarithmic coordinates are bigger that 1/2 as expected for processes involving diffusion of electroactive species, but less than one as expected for processes involving adsorbed electroactive species; this suggest that the formation of the first two peaks is the result of some complex charge transfer processes involving both soluble and adsorbed (or at least immobilized on the electrode) reactants.

Conversely, the frequency shift of quartz crystal resonator has a more complicated behavior. During the initial reduction scan there is a frequency decrease even in the potential range when a noticeable current peak is not present. As indicated by the Sauerbrey equation (5.1), the decrease of the frequency denotes an increase of the mass of the electrode. Further, on the potential range where the first voltammetric cathodic peak is present, there is an important mass loss. During the initial stages of oxidation scan a small mass increase is noticeable in a potential domain in which any voltammetric peak is absent, but the first anodic peak takes place with a more important mass increase, while the second anodic peak takes place with a very important mass loss, process that continues during the initial stages of the final reductive scan.

In order to attempt a quantitative evaluation, the scanned potential range was divided in six potential windows in which a possible individual process takes place.

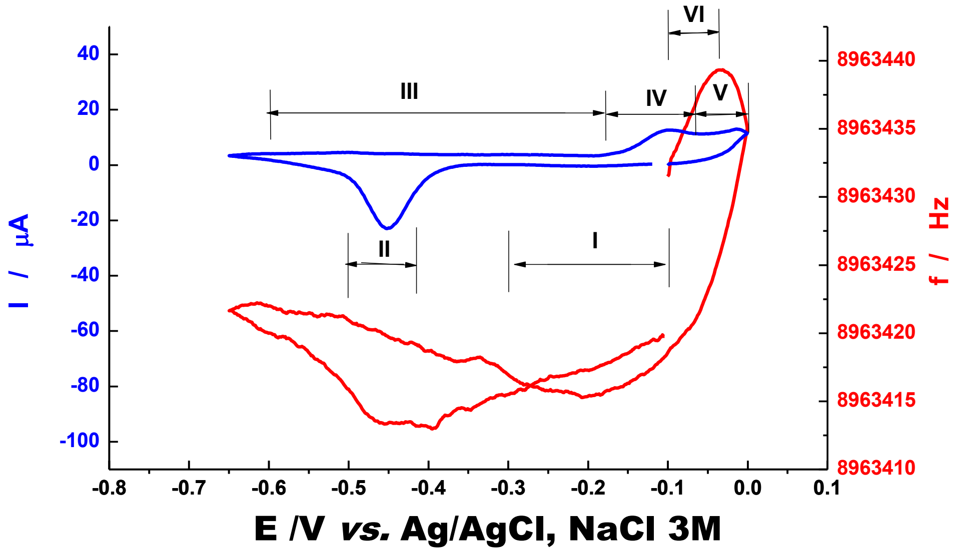


Fig. 5.4 The electrode behavior in different areas of potential

Table 5.1 Electrogravimetric parametres for pH=8.89 and v=2mV s^{-1} scan rate.

Zone	ΔQ	Δm	M/z
	(μC)	(μg)	(g/ mol)
I	-340	9.73	2.7
II	-438	-3.72	-0.8
III	-767	14.9	1.9
IV	81.9	-4.09	-4.8
V	34.4	-22.70	-62.8
VI	-28.7	15.09	50.7

Zone **I**, in which the charge is transferred without formation of a voltammetric peak, could easily be confused with a capacitive zone. But the important mass increase is a strong indication that a faradaic process occurs. More likely is the underpotential hydrogen formation, a process in which the hydrogen obtained remains adsorbed as a monolayer on the interface.

Zone **II** includes the cathodic peak and takes place with a very modest mass decrease. Due to the difficult kinetics, it is unlikely that hydrogen evolution would take place at potentials larger than -0.5V. More reasonable is to assume the oxygen reduction

or oxygen reduction with some involvement of adsorbed hydrogen obtained in zone **I** take place. Only these two possibilities predict correctly the influence of pH on the cathodic peak parameters.

Zone **III** does not contain a voltammetric peak but the mass increase is yet important. The charge involved in **III** is more than twice that of **I**. More likely another reduction process with higher M/z is also involved, but the obtained experimental data make difficult a complete identification.

Zone **IV** includes the first anodic peak and takes place with significant mass decrease. Even more important mass decrease takes place in zone **V**, zone that includes the second anodic peak.

Such important anodic mass decreases can be only asserted taking into consideration copper oxidation or oxidation with formation of a soluble copper complex.

Finally, the last cathodic zone, **VI**, takes place with important mass increase. Combination of following reductions could be assigned:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad M/z = 64\ g\ mol^{-1} \tag{5.9}$$

$$\left[Cu\left(CO_3\right)_2\right]^{2-} + 2e^- \rightarrow Cu + 2CO_3^{2-} \qquad M/z = 64\ g\ mol^{-1} \tag{5.10}$$

$$CuCO_{3(s)} - 2e^- \rightarrow Cu + CO_3^{2-} \qquad M/z = -60\ g\ mol^{-1} \tag{5.11}$$

$$2CuCO_{3(s)} - 2e^- \rightarrow Cu_2CO_{3(s)} + CO_3^{2-} \quad M/z = -30\ g\ mol^{-1} \tag{5.12}$$

in which reactions (5.9) or (5.10) have the most important contribution.

References

1. F. A. Hanc-Scherer, A. Nicoară, C*oupled voltammetric and electrogravimetic investigation of copper behavior in carbonate-bicarbonate solutions*, Studia UBB Chemia, **2013**, 4, 183-191.
2. M. Jitaru, D.A. Lowy, M. Toma, B. C. Toma, L. Oniciu, *Electrochemical reduction of carbon dioxide on flat metallic cathodes*, J. of Appl. Electrochem., **1997**, 27, 875-889.
3. M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, T. Sakata, *Electrochemical Reduction of Carbon Dioxide on Various Metal Electrodes in Low -Temperature Aqueous* $KHCO_3$ *media, J.* Electroanal. Chem., **1990**, 137, 1772.
4. Y. Hori, K. Kikuchi, S. Suzuki, *Production of CO and* CH_4 *in electrochemical reduction of* CO_2 *at metal electrodes in aqueous hydrogencarbonate solution*, Chemistry letters, **1985,** pp. 1695-1698.
5. Y. Hori, K. Kikuchi, S. Suzuki, *Production of CO and* CH_4 *in electrochemical reduction of* CO_2 *at metal electrodes in aqueous hydrogencarbonate solution*, Chemistry letters, **1985,** pp. 1695-1698.
6. J. Lee, Y. Tak, *Electrocatalytic activity of Cu electrode in electroreduction of* CO_2 Electrochim. Acta, **2001**, 46, 3015-3022.
7. V. S.J. Craig, M. Plunkett, *Determination of coupled solvent mass in quartz crystal microbalance measurements using deuterated solvents*, J. of Colloid and Interf. Science **2003**, 262, 126–129.
8. B. I. Lemon, J.T. Hupp, *Electrochemical Quartz Crystal Microbalance Studies of Electron Addition at Nanocrystalline Tin Oxide/Water and Zinc Oxide/Water Interfaces: Evidence for Band-Edge-Determining Proton Uptake*, J. Phys. Chem. B, **1997,** 101, 2426-2429.
9. F. Deng, S. Chen, *Electrochemical Quartz Crystal Microbalance Studies of the Rectified Quantized Charging of Gold Nanoparticle Multilayers*, Langmuir **2007**, *23*, 936-941.
10. W. Visscher, J. F. E. Gootzen, A.P.Cox and J.A. R. van Veen, *Electrochemical quartz crystal microbalance measurements of CO adsorption and oxidation on Pt in various electrolytes*, Electrochim. Acta, **1998**, 43, 533-547.
11. A. Nicoara, *Electrochemical and electrogravimetrical investigation of ZnS thin film electrodeposition*, Studia UBB Chemia, **2004**, *49*, 65-76.

12. Y. Hori, A. Murata, R. Takahashi, *J. Chem. Soc. Faraday Trans.*, **1989**, *185*, 2309.

6. ELECTROCHEMICAL REDUCTION OF CO_2 IN AN APROTIC SOLVENT (IONIC LIQUID) ON SINGLE-CRYSTAL PLATINUM ELECTRODES [1, 2]

The experiments were carried out in an electrochemical cell (**Fig. 6.2**) with three electrodes. The working electrode was Pt single crystal [Pt (100) Pt (110) and Pt (111)] (**Fig. 6.3**), the counter electrode and the reference electrode were 2 Pt wires. The measurements were carried out using a computer controlled potentiostat. The potential of the working electrode was measured against a Pt wire. Experiments were performed at room temperature and atmospheric pressure. In these experiments we used the following gases: Ar and $CO_2 \geq$ 99,998 and a strong acid bis (trifluoromethane) sulfonimide - **H [NTf$_2$].**

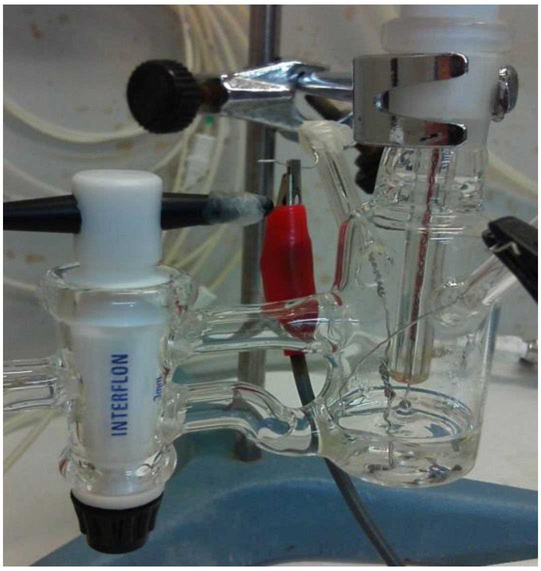


Fig. 6.2 The electrochemical cell used in the experiments.

Fig. 6.3 Pt single crystal

The ionic liquid 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide **[C$_2$mim][NTf$_2$]** Aldrich 98% was chosen because CO_2 has the best solubility [11, 12, 13]. Before each experiment the electrochemical cell (**Fig. 6.2**) has been cleaned and the working electrode, Pt single crystal [Pt (100) Pt (110) and Pt (111)] was made by the method developed by Clavilier [14-16]. Preparation of working electrodes for the identification of surface defects and the degree of cleaning was carried out by 20-30s flame-heating and chilling in a flask with ultrapure water, in which the H_2 and Ar was bubbled in 1:3 ratio [14].

6.3.1 Cyclic voltammograms obtained on single crystals of Pt (hkl) in [C_2mim] [NTf_2]

To identify the electrochemical stability of IL were performed cyclic voltammetry experiments under Ar atmosphere between 0.0V and 3.1V **Fig. 6.6.**

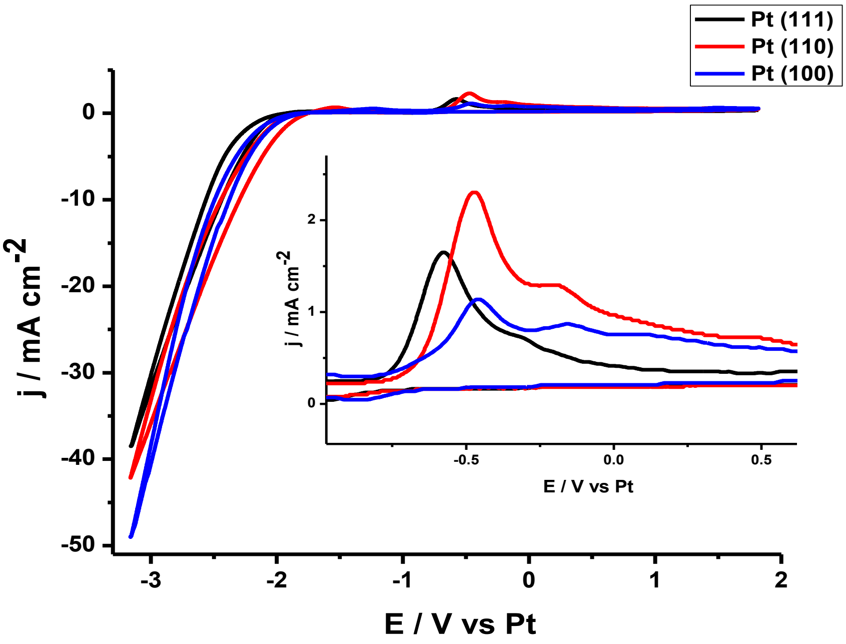


Fig. 6.6 Cyclic voltammograms for Pt single crystal in [C_2mim] [NTf_2] under Ar atmosphere, scan rate 50 mV/s

Starting with a potential of -1.8V a cathodic current was observed and may be associated with reduced imidazolium cation [C2mim]$^+$ to carbene [32]. In the area of the anode is also observed the appearance of a peak (-0.5V) corresponding to the oxidation of the new chemical species formed in the cathode region. The presence of the oxidation peaks shows the formation of the carbenes in the cathode region. According to the literature carbene may be precursor to obtain the products of C1 and C2 [34].

6.3.2 Cyclic voltammograms obtained on single crystals of Pt (hkl) in [C_2mim] [NTf_2] and CO_2

Cyclic voltammograms performed in [C_2mim] [NTf_2] saturated with CO_2 showed the presence of a shoulder in the potential range -2.75V -3V corresponding to CO_2 reduction (**Fig. 6.8**). The potential of CO_2 reduction corresponds with the values in literature [9, 10], where the reduction of CO_2 in the ionic liquid requires very negative potentials.

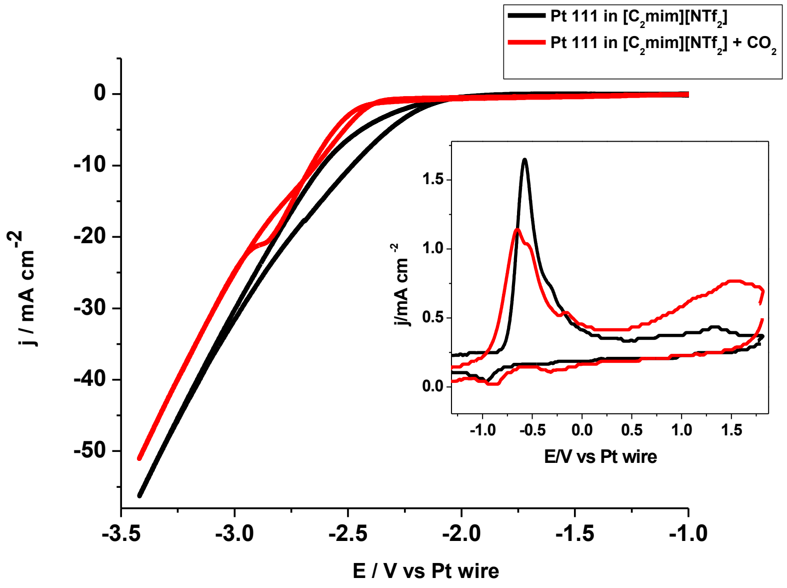


Fig. 6.8. Cyclic voltammograms on Pt single crystals [C_2mim] [NTf_2] saturated with CO_2, scan rate 50 mV/s.

In the anode (see insert **Fig. 6.8**) two oxidation peaks have been identified. The first peak of oxidation observed at-0.5V was associated with the oxidation of the new chemical species formed in the cathodic region. The second anodic peak (1.25V) is not well defined and may be associated with the CO electrooxidation. This peak is better shown for Pt (111) electrode where the electrochemical reduction of CO_2 (shoulder observed) is clearer.

6.3.3 Cyclic voltammograms obtained on single crystals of Pt (hkl) in [C_2mim] [NTf_2], H[NTf_2] and CO_2

In non-aqueous solutions on Pt electrodes, CO_2 is electrochemical reduced to CO according to reaction [35]:

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \qquad (6.2a)$$

$$CO_2^{\bullet -} + CO_2 + e^- \rightarrow CO + CO_3^{2-} \qquad (6.2b)$$

Carbon monoxide obtained by the reduction is not the only product on electrode in non-aqueous solvents. Recent studies show that CO_2 can be reduced electrochemically to formic acid in ionic liquid. The presence of proton is needed to obtain formic acid. Reactions underlying the formation of formic acid are the following [9]:

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \qquad (6.3)$$

$$CO_2^{\bullet -} + H^{\bullet} \rightarrow HCO_2^- \qquad (6.4)$$

$$HCO_2^- + H^+ \leftrightarrow HCOOH \qquad (6.5)$$

From the above observations that the formation of formic acid in ionic liquids is conditioned by the presence of species capable of providing hydrogen (atomic and proton). The use of aqueous solutions as a source of protons is disadvantageous as it leads to contamination of ionic liquid. In the experiments conducted was used as the source of protons a strong acid bis (trifluoromethane) sulfonimide (H [NTf2]). Cyclic voltammograms obtained for the three electrodes of Pt (hkl) in the presence of H [NTf2] are shown in **Fig. 6.9.**

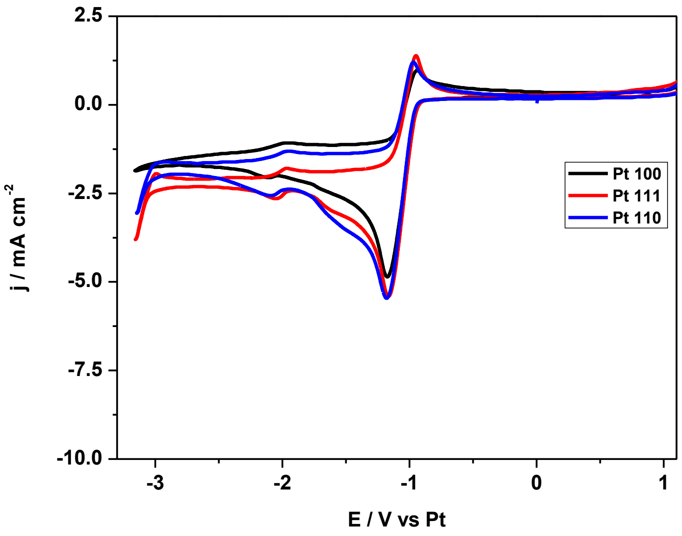


Fig. 6.9 Cyclic voltammograms for Pt single crystal in the presence of H[NTf_2], scan rate 50 mV/s.

In the system consisting of ionic liquid- acid, carbon dioxide was bubbled for 10 minutes; cyclic voltammograms obtained are shown in **Fig. 6.10**.

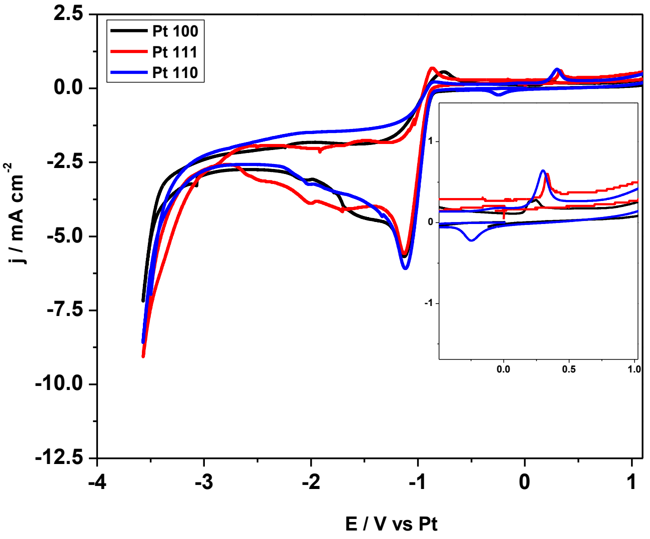


Fig. 6.10. Cyclic voltammograms for Pt single crystal in $[C_2mim][NTf_2]$ + $H[NTf_2]$ + CO_2, scan rate = 50 mV/s between-3.5V and 1.8V.

At more negative potentials voltammograms (see inset **Fig. 6.10**) showed a little oxidation peak (~0.3V) assigned to HCOOH oxidation [9]. The formic acid oxidation peak increases with the extension to more negative values of the potential. This confirms the formation of formic acid in the cathodic area and the catalytic activity of formic acid in the oxidation follows the same trend as in the case of CO electrooxidation as will be explained in chapter 7 [2]. The activity of Pt single crystals follows the order:

Pt(110) > Pt(111) > Pt(100)

The reason why the catalytic activity of the formic acid oxidation is the same as in the case of CO oxidation, can be explained by the fact that the formation of CO is an intermediate step in the oxidation of HCOOH. The oxidation of formic acid may be done in 2 ways.

The first route involves direct oxidation of formic acid to CO_2 [35]

$$HCOOH + Me \rightarrow CO_2 + 2H^+ + Me + 2e^- \qquad (6.9)$$

(Me=Pt, Pd etc)

A second way "indirect path" occurs when the carbon monoxide is adsorbed on the metal surface, followed by two steps:

$$HCOOH + Me \rightarrow Me\text{-}CO + H_2O \qquad (6.10)$$

$$Me + H_2O \rightarrow Me\text{-}OH + H^+ + e^- \qquad (6.11)$$

$$Me\text{-}CO + Me\text{-}OH \rightarrow 2Me + CO_2 + H^+ + e^- \qquad (6.12)$$

References

1. F. A. Hanc-Scherer, C. M. Sánchez Sánchez, E. Herrero, P.Ilea, *Electrochemical CO_2 reduction in room temperature ionic liquids (RTILS) preliminary studies*, **Conference**, **RICCCE18**, September 4-7, **2013**, Sinaia, Romania, Oral presentation.
2. F. A. Hanc-Scherer, C. M. Sánchez-Sánchez, P. Ilea, E. Herrero, *Surface-Sensitive Electrooxidation of Carbon Monoxide in Room Temperature Ionic Liquids*, ACS Catal. **2013**, 3, 2935−2938.
3. K. Tamura, S.Miyaguchi , K. Sakaue, Y. Nishihata, J. Mizuki, *Direct observation of Au(111) electrode surface structure in bis(trifluoromethylsulfonyl)amide-based ionic liquids using surface X-ray scattering*, Electrochemistry Communications, **2011**, 13, 411–413.
4. R. Atkin, N. Borisenko, M. Druschler, S. Z. El Abedin, F. Endres, R. Hayes, B. Huber and B. Roling, *An in situ STM/AFM and impedance spectroscopy study of the extremely pure 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate/Au(111) interface: potential dependent solvation layers and the herringbone reconstruction*, Phys. Chem. Chem. Phys., **2011**, 13, 6849–6857
5. L. Anicai, A. Petica, S. Costovici, P. Prioteasa, T. Visan, *Electrodeposition of Sn and NiSn alloys coatings using choline chloride based ionic liquids—Evaluation of corrosion behavior*, Electrochimica Acta, **2013**, 114, 868–877
6. W. Wang, Y. Ji, H. Xu, H. Li, T. Visan, F. Golgovic, *A high packing density micro-thermoelectric power generator based on film thermoelectric materials fabricated by electrodeposition technology*, Surface and Coatings Technology, **2013**, 231, 583–589
7. R. A. Di Leo, A. C. Marschilok, K. J. Takeuchi, E. S. Takeuchi, *Battery electrolytes based on saturated ring ionic liquids: Physical and electrochemical properties,* Electrochimica Acta **2013**, 109, 27–32
8. X. Li, Y. Liu, L. Zheng, M. Dong, Z. Xue, X. Lu, X. Liu, *A novel nonenzymatic hydrogen peroxide sensor based on silver nanoparticles and ionic liquid functionalized multiwalled carbon nanotube composite modified electrode*, Electrochimica Acta, **2013**, 113, 170–175
9. B. C. M. Martindale, R. G. Compton, *Formic acid electro-synthesis from carbon dioxide in a room temperature ionic liquid*, Chem. Commun., **2012**, 48, 6487–6489

10. L. L. Snuffin, L. W. Whaley, L. Yu - *Catalytic Electrochemical Reduction of CO2 in Ionic Liquid EMIMBF3Cl*, Journal of The Electrochemical Society, **2011**, 158, 155-158
11. Cesar Cadena, Jennifer L. Anthony, Jindal K. Shah, Timothy I. Morrow, Joan F. Brennecke, and Edward J. Maginn, *J. Am. Chem. Soc*. **2004**, 126, 5300-5308
12. Ying Hou and Ruth E. Baltus, *Ind. Eng. Chem. Res.* **2007**, *46,* 8166-8175
13. Surya S. Moganty and Ruth E. Baltus, , *Ind. Eng. Chem. Res.* **2010**, *49,* 5846–5853
14. Clavilier, J., Flame-annealing and cleaning technique, in: *Interfacial Electrochemistry: Theory, Experiment, and Applications*, A. Wieckowski (ed.), Marcel Dekker: New York, **1999**, p. 231.
15. Clavilier, J., R. Faure, G. Guinet, R. Durand, *Preparation of monocrystalline platinum microelectrodes and electrochemical study of the plane surfaces cut in the direction of the {111} and {110} planes*, J Electroanal Chem, **1980**, 107, 205.
16. Clavilier, J., *The role of anion on the electrochemical behavior of a {111} platinum surface: An unusual splitting of the voltammogram in the hydrogen region*, *J* Electroanal Chem, **1980**, 107, 211.
17. Funtikov A. M., U. Stimming, R. Vogel, *Anion adsorption from sulfuric acid solutions on Pt(111) single crystal electrodes*, J Electroanal Chem, **1997,** 428, 147.
18. Garcia-Araez N., V. Climent, P. Rodriguez, J. M. Feliu, *Thermodynamic analysis of (bi)sulphate adsorption on a Pt(111) electrode as a function of pH*, Electrochim Acta, **2008**, 53, 6793.
19. Saravanan, C., M. T. M. Koper, N. M. Markovic, M. Head-Gordon, P. N. Ross, *Modeling base voltammetry and CO electrooxidation at the Pt(111)-electrolyte interface:Monte Carlo simulations including anion adsorption*, Phys Chem Chem Phys, **2002**, 4, 2660.
20. Lebedeva, N. P., M. T. M. Koper, E. Herrero, J. M. Feliu, R. A. van Santen, *CO oxidation on stepped Pt[n(111)x(111)] electrodes*, J Electroanal Chem, **2000**, 487, 37.
21. Climent et al., *Russ. J. Elec.*, Vol. 42, (2006): p. 1145
22. Kolb D. M., *Surface reconstruction at metal-elecrolyte interfaces*, *in: Structure of Electrified Interfaces*, J. Lipkowski, and P. N. Ross, (eds.), VCH: New York, **1993**, 65.
23. Markovic N. M., B. N. Grgur, C. A. Lucas, P. N. Ross, *Surface electrochemistry of CO on Pt(110)-(1x2) and Pt(110)-(1x1) surfaces*, Surf Sci, **1997**, 384, 805.

24. Lopez-Cudero, A., A. Cuesta, C. Gutierrez, *Potential dependence of the saturation CO coverage of Pt electrodes: The origin of the pre-peak in CO-stripping voltammograms. Part 2: Pt (100)*, J Electroanal Chem, **2006**, 586, 204.
25. *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH Verlag, Weinheim, **2003**.
26. H. Ohno, *Electrochemical aspects of ionic liquids*, Wiley VCH Verlag, **2011.**
27. U. Schroder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z. Suarez, C. S. Consorti, R. F. de Souza and J. Dupont, New J. Chem., **2000**, 24, 1009–1015
28. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, Inorg. Chem., **1996**, 35, 1168–1178
29. Maaike C. Kroon, Wim Buijs, Cor J. Peters and Geert-Jan Witkamp, Green Chemistry, **2006**, 8, 241-245
30. George H. Lane, Electrochimica Acta **2012**, 83, 513– 528
31. A. A. M. Beigi, M. Abdouss, M. Yousefi, S. M. P., A. Vahid, J. Molecular Liquids, 2013, 177, 361-368
32. B. Gorodetsky, T. Ramnial, N. R. Branda, J. A. C. Clyburne, Chem. Commun., **2004**, 1972-1973
33. Adriana M. Navarro-Suarez, Jonnathan C. Hidalgo-Acosta, Luca Fadini, Juan M. Feliu and Marco F. Suarez-Herrera, The Journal of Physical Chemistry, **2011**, 115, 11147-11155
34. S. Wasmus, E. Cataneo , W. Vielstich, Electrochimica Acta, **1990**, 35, 771-775
35. K. Izutsu, *Electrochemistry in Nonaqueous Solutions*, Wiley-VCH Verlag GmbH & Co. KGaA, **2002.**
36. D. S. Silvester, L. Aldous, C. Hardacre, R. G. Compton, *An Electrochemical Study of the Oxidation of Hydrogen at Platinum Electrodes in Several Room Temperature Ionic Liquids*, *J. Phys. Chem. B,* **2007**, *111*, 5000-5007.
37. R. V. Niquirilo, E. Teixeira-Neto, G. S. Buzzo, H. B. Suffredini, *Int. J. Electrochem. Sci*., **2010**, 5, 344-354.

7. ELECTROOXIDATION OF CARBON CARBON IN IONIC LIQUIDS [1]

Cyclic voltammetry experiments were carried out in the potential range of 1.0V -1.8V in the absence and presence of CO_{ads}. **Fig. 7.3** corresponding to the electrochemical oxidation of CO adsorbed layer (COads) on the Pt electrode (hkl).

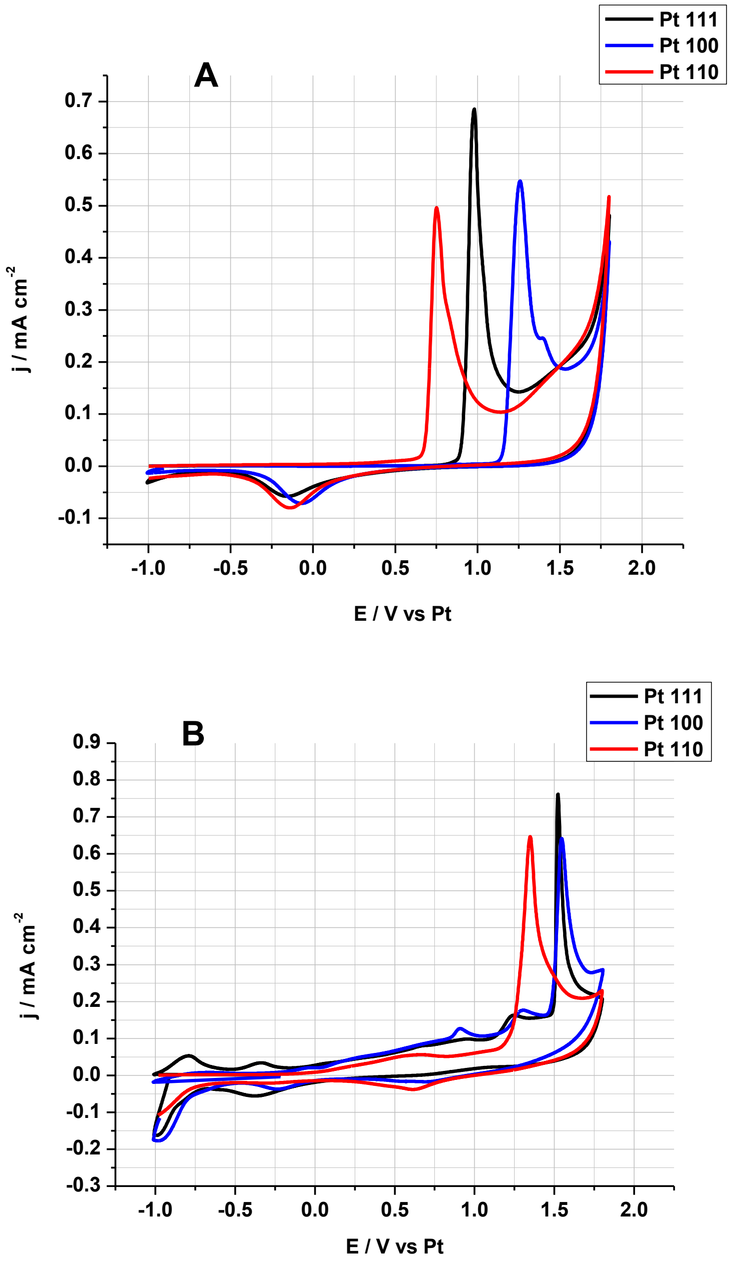


Fig. 7.3 Oxidation of CO on Pt single crystal electrodes in A) $[C_2mim][BF_4]$ and B) $[C_2mim][NTf_2]$. Scan rate = 50 mV/s

Fig. 7.3 shows clear evidence of the surface-sensitive nature of the electrooxidation of CO in [C_2mim][BF_4] and [C_2mim][NTf_2] because of the different peak potential for the reaction displayed by each Pt(hkl) electrode studied here.

In all cases, a more positive potential for the electrooxidation of CO_{ads} in [C_2mim][NTf_2] is necessary. This is probably due to its higher hydrophobicity in comparison with [C_2mim][BF_4], which inhibits the hydroxyl radicals($OH^{\bullet -}$) adsorption on the platinum surface, postulated in aqueous media as the keystone step for completing the CO oxidation reaction, according to reaction 7.1:

$$CO_{ads} + OH_{ads} \rightarrow CO_2 + H^+ + e^- \qquad (7.1)$$

The presence of hydroxyl groups is due to contaminated water in ionic liquid. The oxidation in ionic liquids studied takes place at a more positive potential than in aqueous media [6], on the one hand due to the absence of competing oxidation reaction of the water and on the other hand due to the oxidative stability of the anion forming IL [7 8].

The reactivity trend Pt(100) < Pt(111) < Pt(110) reported here for the studied ILs is consistent with some results previously reported in the literature using highly acidic aqueous solutions (the case is most comparable to the use of ILs, since there is a shortage of OH radicals in both media) in which the catalytic activity toward the CO oxidation was reported to increase in the same way Pt(100) < Pt(111) < Pt(110). In contrast, when a much larger amount of OH radicals was available in aqueous solution (pH > 3), there was a change in the catalytic activity toward CO oxidation, with Pt(111) as the least active crystallographic plane of platinum.

The current recorded in [C_2mim][NTf_2] for all 3 electrodes is much greater than [C_2mim] [BF_4] (**Fig. 7.3**) this is due to the [C_2mim] [NTf_2] viscosity (half viscosity value [C_2mim] [BF_4] [10]) that promote the production of higher currents. The potential of the peak and the amount of charge (measured by integration) are shown in **Table 7.1**.

Table 7.1. Peak Potential and Integration Charge Enclosed within the CO Oxidation Peak at the Corresponding Pt(hkl) Electrodes

Ionic liquid	**Electrode**	**E_{peak}**	**Q**
		(V vs Pt)	**(μC/cm^2)**
[C_2mim][NTf_2]	Pt (110)	0.75	1856

	Pt (111)	0.98	1968
	Pt (100)	1.26	2142
[C_2mim][BF_4]	Pt (110)	1.35	4432
	Pt (111)	1.53	4590
	Pt (100)	1.55	5129

There is a clear shift in peak potentials for CO_{ad} oxidation when comparing [C_2mim][BF_4] and [C_2mim][NTf_2] (0.6 V for Pt(110), 0.55 V for Pt(111), and 0.29 V for Pt(100) electrodes) as a result of the presence of a different anion.

The charge values associated with CO electrooxidation on both ILs included in Table **7.1** present much larger values than a conventionally associated oxidation charge for the CO_{ad} in aqueous media (~300 $\mu C/cm^2$) [11] for the same Pt(hkl) electrodes. This fact points out that stripping voltammetries presented here also include the concomitant oxidation of the corresponding IL anion, which we believe is promoted by the presence of CO_{ad} on the electrode.

Thus, the nature of the RTIL anion strongly affects the Pt(hkl) reactivity in these media. The Pt(110) electrode oxidizes CO_{ad} at 0.75 V (**Fig. 7.3.A**), but at this potential in **Fig. 7.3.B** an adsorption phenomenon appears that is associated with the $NTf2^-$ anion presence that blocks this active site for CO_{ad} oxidation. In contrast, this is available when $BF4^-$ is the RTIL anion.

The (100) plane seems to have the lowest activity on the Pt surface in both ILs, since the peak potential is the highest compared for all three basal planes.

In conclusion, we present here relevant results for energy storage and heterogeneous catalysis fields because CO adsorption represents the common poisoning step in many oxidative reactions employed in synthesis and different energy sources, such as fuel cells. We demonstrated that electrooxidation of CO at the Pt(hkl)-IL interface represents a surface-sensitive process that exhibits different catalytic activity following the reactivity order Pt(110) > Pt(111) > Pt(100) in both RTILs. Thus, increasing the number of (110) sites on the surface of the platinum catalyst, by using proper capping agents during the synthesis, represents the next goal to achieving highly active catalysts for the CO electrooxidation reaction in ILs. Furthermore, we proved the important effect of the nature of the IL anion, since it competes for the active site at the catalyst surface, controlling the overpotential required to complete the electrooxidation of CO_{ad}.

References

1. F. A. Hanc-Scherer, C. M. Sánchez-Sánchez, P. Ilea, E. Herrero, *Surface-Sensitive Electrooxidation of Carbon Monoxide in Room Temperature Ionic Liquids*, ACS Catalysis, **2013**, 3, 2935−2938
2. E. O. Barnes, A. M. O'Mahony, L. Aldous, C. Hardacre, R. G. Compton, *The electrochemical oxidation of catechol and dopamine on platinum in 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_2$mim][NTf$_2$]) and 1-Butyl-3-methylimidazolium tetrafluoroborate ([C$_4$mim][BF$_4$]): Adsorption effects in ionic liquid voltammetry,* J. Electroanal. Chem. **2010**, 646, 11−17
3. A. M. Navarro-Suarez, J. C. Hidalgo-Acosta, L. Fadini, J. M. Feliu, M. F Suarez-Herrera, *Electrochemical Oxidation of Hydrogen on Basal Plane Platinum Electrodes in Imidazolium Ionic Liquids*, J. Phys. Chem., **2011**, 115, 11147−11155
4. C. M. Sánchez-Sánchez, J. Souza-Garcia, E. Herrero, A. Aldaz, *Electrocatalytic reduction of carbon dioxide on platinum single crystal electrodes modified with adsorbed adatoms*, Journal of Electroanalytical Chemistry, 2012, 668, 51-59.
5. C.M. Sánchez-Sánchez, F.J. Vidal-Iglesias, J. Solla-Gullón, V. Montiel, A. Aldaz, J.M. Feliu, E. Herrero, *Scanning electrochemical microscopy for studying electrocatalysis on shape-controlled gold nanoparticles and nanorods,* Electrochimica Acta, 2010, 55, 8252-8257.
6. H. Kita, H. Naohara, T. Nakato, S.Taguchi, A. Aramata, *Effects of adsorbed CO on hydrogen ionization and CO oxidation reactions at Pt single-crystal electrodes in acidic solution*, Journal of Electroanalytical Chemistry, **1995**, 386, 197–206.
7. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts,* Inorg. Chem., **1996**, 35, 1168–1178.
8. M. C. Kroon, W. Buijs, C. J. Peters, G-Jan Witkamp, *Decomposition of ionic liquids in electrochemical processing*, Green Chem., **2006**, 8, 241–245.
9. R. Gisbert, G. Garcia, M. T. M. Koper, *Oxidation of carbon monoxide on poly-oriented and single-crystalline platinum electrodes over a wide range of pH*, Electrochimica Acta, **2011**, 56, 2443-2449.

10. B. Kirchner, *Topics in Current Chemistry. Ionic Liquids vol. 290,* Springer, Heidelberg, **2010**.
11. E. Herrero, B. Alvarez, J. M. Feliu, S. Blais, Z. Radovic-Hrapovic, G. Jerkiewicz, *Temperature dependence of the* CO_{ads} *oxidation process on Pt(1 1 1), Pt(1 0 0), and Pt(1 1 0) electrodes,* J. Electroanal. Chem., **2004**, 567, 139-149.

8. CATHODIC REDUCTION OF CO_2 ON LEAD ELECTRODE-CYCLIC VOLTAMMETRY [1]

To highlight the cathodic reduction of CO2, cyclic voltammetry (CV) studies were carried out at lead electrode. The reactions that occurred on lead electrode in alkaline media at 25°C and their electrochemical potential vs standard hydrogen electrode (SHE) are shown below [8]:

$CO_2(aq) + H_2O + 2e^- \rightarrow HCOO^- + OH^-$ $E^o = -1.02$ V/ENH (8.1)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^o = -0.83$ V/ENH (8.2)

In order to study the carbon dioxide electrochemical reduction first experiments were performed using Na_2CO_3 0.5M (deaerated by bubbling Ar) and saturated with CO_2 (**Fig. 8.1**).

In the presence of carbonate ions a wave is observed at a potential of ca. -1.45 V/ Ag/AgCl/KClsat due to reduction of the ions. When CO_2 is bubbled a well-defined reduction peak is observed at -1.6V due to CO_2 reduction.

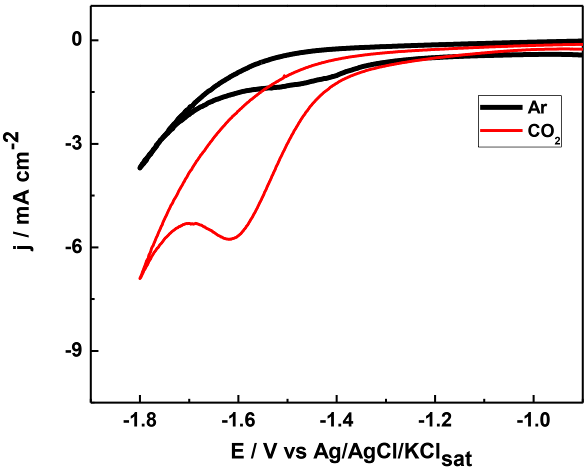


Fig. 8.1. Cyclic voltammograms on Pb electrode at 50 mV/s in 0.5 M Na_2CO_3 with and without CO_2.

The current density peak (-5.6 mA/cm2) for CO_2 reduction to formate is close to the data from literature [9, 10].

Based on cyclic voltammetry data the current efficiency (CE) can be estimated for each type of electrolyte by dividing the amount of charge consumed for ERCD (Q_{ERCD}) to total amount of charge consumed (Qtot) as described in **Table 8.1**

Table 8.1. Current efficiency evaluated by CV measurements for different types of electrolytes

Type of electrolyte	**pH**	**Q_{tot}**	**Q_{ERCD}**	**RC**
		(mAs)		**(%)**
Na_2CO_3(0.5M) + CO_2	10.6	10.4	4.0	38
Na_2SO_4 (0.6M)+ CO_2	6.3	12.8	7.9	62
Na_2SO_4(0.6M)+Na_2CO_3(0.1M) + CO_2	7.5	8.7	5.0	58

From the values presented in **Table 8.1** it can be seen the electrolyte solution saturated with CO_2 is beneficial to the process regardless of the type of electrolyte.

References

1. F. A. Hanc-Scherer, P. Ilea, *Electrochemical Reduction of CO2 on lead Electrode. I. Cyclic Voltammetry and Long Time Electrosynthesis Studies*, Studia UBB Chemia, **2013**, 3, 75-84.
2. M. Jitaru, D.A. Lowy, M. Toma, B. C. Toma, L. Oniciu, *Electrochemical reduction of carbon dioxide on flat metallic cathodes*, Journal of Applied Electrochemistry, **1997**, 27, 875-889.
3. C. M. Sánchez-Sánchez, V. Montiel, D. A. Tryk, A. Aldaz, and A. Fujishima, *Electrochemical approaches to alleviation of the problem of carbon dioxide accumulation*, Pure and Applied Chemistry, **2001**, Vol. 73, No. 12, 1917–1927.
4. R.P.S. Chaplin, A.A. Wragg, *Effects of process conditions and electrode material on reaction pathways for carbon dioxide electroreduction with particular reference to formate formation*, Journal of Applied Electrochemistry, **2003**, 33, 1107–1123.
5. B. Eneau-Innocent, D. Pasquier, F. Ropital, J.-M. Léger, K.B. Kokoh, *Electroreduction of carbon dioxide at a lead electrode in propylene carbonate: A spectroscopic study*, Applied Catalysis B: Environmental, **2010**, 98, 65–71.
6. Y. Hori, "*Electrochemical CO2 reduction on Metal Electrodes". Modern Aspects of Electrochemistry*, Number 42, Springer, New York, **2008**.
7. Allen J. Bard, *Encyclopedia of Electrochemistry of the Elements*, Marcel Dekker, Inc. New York and Basel, **1973**, Volume IX, Part A.
8. H. Li, C. Oloman, *Development of a continuous reactor for the electro-reduction of carbon dioxide to formate – Part 1: Process variables*, Journal of Applied Electrochemistry, **2006** 36, 1105–1115.
9. Y. Hori, K. Kikuchi, S. Suzuki, *Production of CO and CH4 in electrochemical reduction of CO2 at metal electrodes in aqueous hydrogencarbonate solution*, Chemistry letters, **1985,** 1695-1698.
10. Y. Hori, H. Wakebe, T.,Tsukamoto, O, Koga, *Electrocatalytic process of CO selectivity in electrochemical reduction of* CO_2 *at metal electrodes in aqueous media*, Electrochimica Acta**, 1994,** 39, 1833-1839.
11. Y. Hori, S. Suzuki, Bulletin of the Chemical Society of Japan, **1982,** 55, 660.

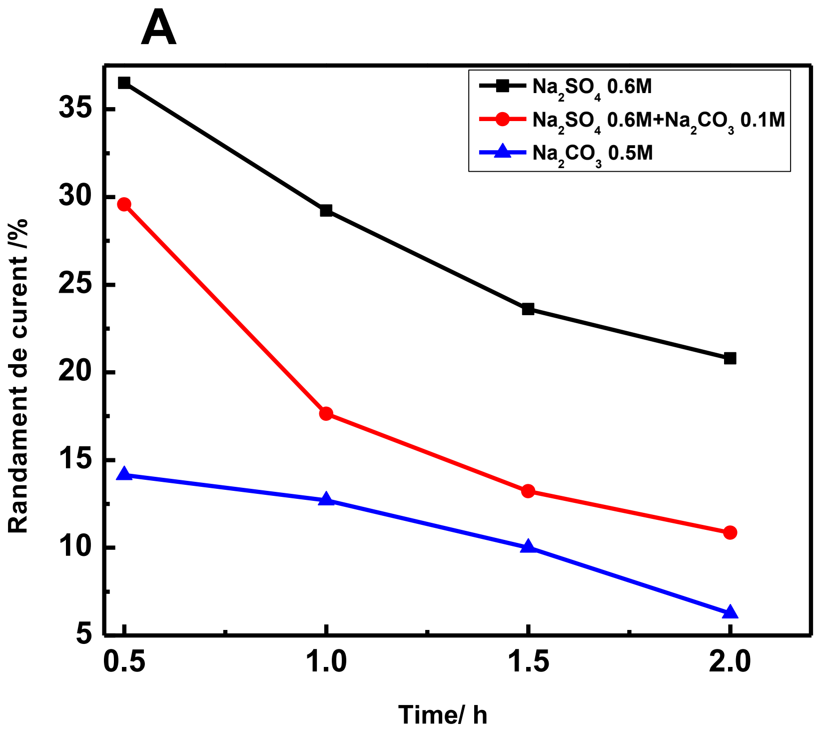
12. B. Innocent, D. Pasquier, F. Ropital, F. Hahn, J.-M. Leger, K.B. Kokoh, *FTIR spectroscopy study of the reduction of carbon dioxide on lead electrode in aqueous medium*, *Applied Catalysis B: Environmental*, **2010,** 94, 219–224.

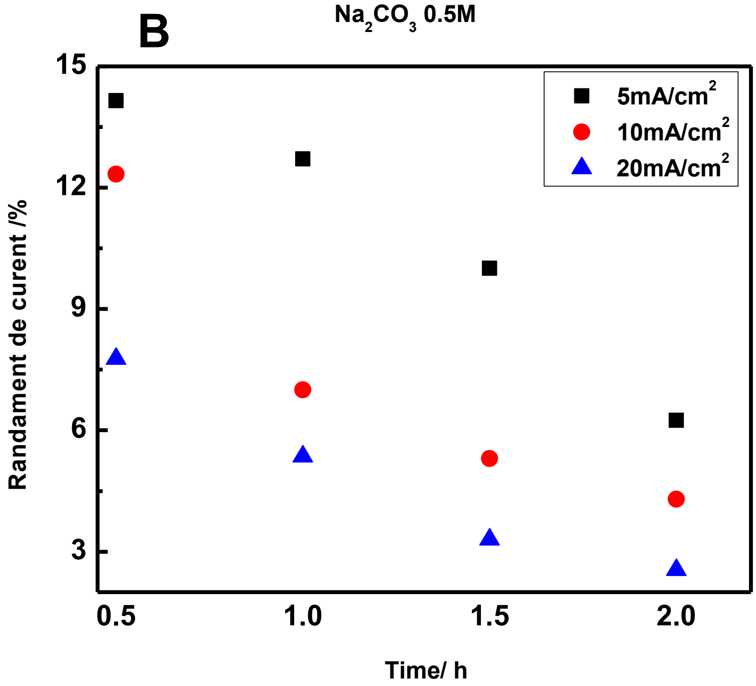
9. ELECTROSYNTHESIS IN A FILTER PRESS REACTOR USING A LEAD CATHODE [1]

In the cathodic compartment of the reactor, CO_2(aq) is reduced to formate according to equation (8.1) in parallel with equation (7.2), while the reaction at anode is (9.1):

$$O_2 + 4H^+ + 4\,e^- \rightarrow 4\,OH^- \qquad E^o=+0.41\ V/SHE \qquad (9.1)$$

Current efficiency (CE) obtained during the electrolysis are shown in **Fig.9.2 A**





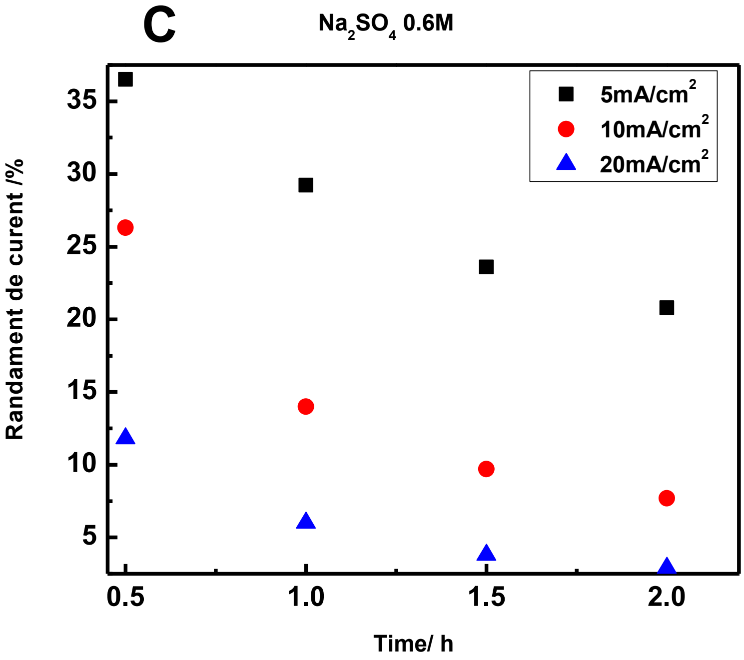


Fig. 9.2 A) current efficiency (CE) obtained during the electrolysis formate in different saturated CO_2 electrolyte current density of 5 mA/cm^2, **B**) 0.5 mol L^{-1} Na_2CO_3 saturated with CO_2 at different current densities, **C**) in 0.6 mol L^{-1} Na_2SO_4 saturated with CO_2 at different current densities.

Changing sulphate anion with carbonate anion or adding carbonate to sulphate solution leads to a decrease in current efficiency **Fig. 9.2 A**. The modification in CE appears to be influenced by changes in pH (what was observed in cyclic voltammetry experiments).

The Na_2CO_3 and Na_2SO_4 0.6M + Na_2CO_3 0.1M solutions have a pH value greater than 10 which makes the reaction (7.1) to be less favourable. In this case adsorbed CO_2 in solution will react with carbonate to bicarbonate according to the reaction (8.3).

The poor current efficiencies obtained in the carbonate presence is due to CO_3^- species whose reaction with CO_2 reaction (8.3) competing reaction (8.1) and leading to an inhibition of the formation of formate.

Measurements were also performed at different current densities (**Fig. 9.2 B** și **C**). As can be observed in **Fig. 9.2 B** și **C,** increasing the current density typically lowers the formate current efficiency. This was observed by Udupa et al. [7] and can be attributed mainly to CO_2 concentration polarization [8]. The experiments undertaken by Koleli et al. [9] on Pb electrode showed a dependence of the formate current efficiency on current density, while results obtained on Sn [10] show an increasing of current efficiency with decreasing current. We observed a similar trend (decreasing in current efficiency with increasing current) for carbonate/sulphate solutions.

Due to the H2-evolution, the current efficiencies for the HCOO- formation decreases with the rising of the electrolysis time.

After 30-45 minutes of electrolysis, a cathode deactivation was observed (the corresponding current efficiencies decreased with 15% in the case of Na2SO4 electrolyte-**Fig. 9.2 A**).

"Poisoning" of the cathode over time has been observed for CO_2 electroreduction on copper electrodes [11-15], and some effects of this deactivation have been indicated on *sp* group (In, Pb, Sn) electrodes. Koleli and al. [16] show that the current efficiency decreased in time during electrolysis thus the highest current efficiency for formic acid production obtained in carbonate solution on Pb after 30 min. was 39% and after 120 min. CE was 10%. Kapusta and al. [17] showed that low efficiency was due to the formation of organometallic complexes on the tin electrode, this situation favouring hydrogen evolution reaction as a competitive reaction.

References

1. F. A. Hanc-Scherer, P. Ilea, *Electrochemical Reduction of CO2 on lead Electrode. I. Cyclic Voltammetry and Long Time Electrosynthesis Studies*, Studia UBB Chemia, **2013**, 3, 75-84
2. S. Ha, C. A. Rice, R. I. Masel, A. Wieckowski, *Methanol conditioning for improved performance of formic acid fuel cells*, Journal of Power Sources, **2002**, 112, 655–659
3. X Wang, J. Hu, I-M. Hsing, *Electrochemical investigation of formic acid electro-oxidation and its crossover through a Nafion® membrane*, Journal of Electroanalytical Chemistry, **2004**, 562, 73–80
4. J-H. Choi, K-J. Jeong, Y. Dong, J. Hanb, T-H. Limb, J-S. Lee, Y.-E. Sung, *Electro-oxidation of methanol and formic acid on PtRu and PtAu for direct liquid fuel cells*, Journal of Power Sources, **2006**, 163, 71–75
5. X. Yu, P. G. Pickup, *Recent advances in direct formic acid fuel cells (DFAFC)*, Journal of Power Sources, **2008**, 182,124–132.
6. F. Albert, N. Barbulescu, C. Holszky, C. Greff, “Analiză chimică organic”, Ed. Tehnica, Bucureşti, **1970**
7. K.S. Udupa, G.S. Subramanian and H.V.K. Udupa, *The electrolytic reduction of carbon dioxide to formic acid*, Electrochimica. Acta, 1971, 16, 1593-1598
8. H. Li, Colin Oloman, *Development of a continuous reactor for the electro-reduction of carbon dioxide to formate – Part 1: Process variables*, Journal of Applied Electrochemistry, **2006** 36,1105–1115
9. F. Koleli, D. Balun, *Reduction of CO_2 under high pressure and high temperature on Pb-granule electrodes in a fixed-bed reactor in aqueous medium*, Applied Catalysis A: General, **2004**, 274, 237-242
10. Hui Li, Colin Oloman, *The Electro-Reduction of Carbon Dioxide in a Continuous Reactor*, Journal of Applied Electrochemistry, **2005**, 35, 955-965
11. D. W. DeWulf, T. Jin, A. J. Bard, *Electrochemical and Surface Studies of Carbon Dioxide Reduction to Methane and Ethylene at Copper Electrodes in Aqueous Solutions* Journal of Electrochemical Society **1989,** 136, 1686-1691
12. S. Wasmus, E. Cattaneo, *Reduction of carbon dioxide to methane and ethene—an on-line MS study with rotating electrodes*, Electrochimica Acta, **1990,** 35, 771-775

13. G. Kyriacou, A. Anagnostopoulos, *Electroreduction of* CO_2 *on differently prepared copper electrodes: The influence of electrode treatment on the current efficiences*, Journal of Electroanalytical Chemistry, **1992,** 322, 233-246.
14. B. Jermann, J. Augustynski, *Long-term activation of the copper cathode in the course of* CO_2 *reduction*, Electrochimica Acta **1994,** 39, 1891-1896.
15. J. Lee, Y. Tak, *Electrocatalytic activity of Cu electrode in electroreduction of* CO_2 Electrochimica Acta, **2001,** 46, 3015-3022.
16. F. Koleli, T. Atilan, N. Palamut, *Electrochemical Reduction of CO2 at Pb-and Sn-Electrodes in a Fixed-Bed Reactor in Aqueous K2CO3 and KHCO3 Media*, Journal of Applied Electrochemistry **2003,** 33, 447-450.
17. S. Kapusta, N. Hackerman, *The Electroreduction of Carbon Dioxide and Formic Acid on Tin and Indium Electrodes*, Journal of the Electrochemical Society, **1983,** 130, 3, 607-613.

10. MASS BALANCE OF THE ELECTROCHEMICAL REACTOR

The experimental research in aqueous solutions has demonstrated that the ERCD is a viable alternative and environmentally compatible recycling methode.

The electrochemical conversion of CO_2 to formate (with concomitant generation of hydrogen) is the solution we propose. Thus the two reduction products - formate and hydrogen - can be used as fuel cell anodic reaction.

The mass balance of the electrochemical reactor was calculated. In the cathodic compartment was Na_2SO_4 1M solution and in the anodic compartment was chosen an aqueous solution of NaOH 3M and 1M Output.

The compartments were separated by a Nafion 324 cation-exchange membrane allowing Na^+ ions crossing the cathode.

For the calculation of the mass balance we consider a production of 68 kg/h NaCOOH pure substance.

The reduction of CO_2 to formate with a current efficiency of 25%, concomitant with the HER with a current efficiency of 75%. In the anodic reaction we obtain oxygen with a current efficiency of 100 %. The voltage across the electrochemical reactor is 2 V.

By solving the equations of balance (which took into account the flow of input and output components be they liquid, gaseous), it could present a mass balance for the anode and cathode compartment.

Table 10.1 Mass balance in the cathodic compartment

Input		**Output**	
Ingredients	**kg/h**	**Ingredients**	**kg/h**
CO_2	132	CO_2	88
H_2O	177	NaCOOH	68
Na_2SO_4	29	NaOH	280
Na+	184	H_2	6
H_2O with Na^+	576	H_2O out	623
		H_2O with cathodic gases	5
		Na2SO4	29
TOTAL	**1099**	**TOTAL**	**1099**

Table 10.2 Mass balance in the anodic compartment

Input		**Output**	
Ingredients	**kg/h**	**Ingredients**	**kg/h**
NaOH	345	O_2	64
H_2O	806	NaOH	25
		H_2O genated	72
		H_2O with oxygen	2
		H_2O output	228
		Na^+	184
		H2O with Na^+	576
Total	**1151**	**Total**	**1151**

The global mass balance on the 2 compartments

Table 10.3 Mass balance on the electrochemical reactor

Input		**Output**	
Ingredients	**kg/h**	**Ingredients**	**kg/h**
CO_2	132	CO_2	88
H_2O	983	NaCOOH	68
Na_2SO_4	29	NaOH	305
NaOH	345	H_2	6
		H_2O output	929
		Na_2SO_4	29
		O_2	64
Total	**1490**	**Total**	**1490**

Based on mass balance it was calculated electricity consumption.

Such consumption is:

Eb * I * t = 429 kWh

The specific energy consumption for NaHCOO = 1.6 kWh / kg

Literature data shows that the values are of approx. 3.8 kWh / kg [1].

The specific energy consumption for H_2 = 53.6 kWh / kg respectively 4.8 kWh / Nm3 H_2

The specific energy consumption for O_2 = 6.7 kWh / kg. Course of interest are hydrogen and sodium formate which can be used as fuel in fuel cells.

11. GENERAL CONCLUSIONS

Electrochemical reduction of CO_2 is attractive both in terms of theory and practice allowing CO_2 reduction and conversion to valuable products.

For electrochemical reduction of CO_2 to be a competitive alternative to overcome the following problems: low solubility of CO_2, HER , the reaction rate decreased .

In the study of literature were analyzed aspects of electrode material (especially electrodes of copper and lead) and how it affects the selectivity of the reduction products. Distribution and yield of the product depends on the potential, temperature, pressure and the electrolyte solution.

Copper electrode material was chosen because it is the only one that can achieve significant yield hydrocarbons and alcohols. On Pb electrodes HCOOH can be obtained which is used in fuel cells.

The study of electrochemical reduction of CO_2 electrode of alkaline copper carbonate and sodium bicarbonate (pH 8.8-10.5) (Chapter 4) was carried out by cyclic voltammetry.

Following measurements evidenced an irreversible process. Electrochemical reduction of CO_2 is a mixed diffusion - adsorption process demonstrated by corelation of log Ip vs. log v.

Cyclic voltammetry investigations allowed the identification of kinetic parameters such as the transfer of an electron and a proton in the rate determining step and a charge transfer coefficient of 0.9.

Using quartz crystal microbalance (Chapter 5) allowed us to identify possible processes occurring at the electrode. The electrochemical reduction of CO_2 on the Cu electrode is a complex process of adsorption desorption and with formation of insoluble species resulting from the blocking of the electrode surface.

Experiments were conducted between -0.1 ÷ - 0.65V and there was no clear evidence of the direct reduction of CO_2. By operating at more negative potential electrochemical reduction of CO_2 can occur and this is encouraged by the presence of a copper electrode surface monolayer of hydrogen, which due to its reactivity may participate in its reduction.

The electrolyte solution can influence the reduction product obtained, as shown in the literature to analyze CO_2 conversion in ionic liquids Pt single crystals (Chapter 6).

Cyclic voltammetry tests showed that [C2mim][NTf2] has a great stability. The presence of CO_2 in the system changes dash voltammograms, which depends on the type of crystal. The product of the reduction of CO_2 in liquid is carbon monoxide.

Experiments conducted in the presence of CO_2 and a strong acid lead to changes in LI voltamograms allure with a small peak observed in anodic oxidation. This peak corresponds to the oxidation of HCOOH (formed in cathodic region). The electrocatalytic activity of the process depends on the type of the crystal orientation in the order:

Pt (110) > Pt (111) > Pt (100)

The presence of formic acid could be detected in most negative potential of - 2.5V , and the formation of CO seems to be an intermediate stage in the production of HCOOH.

Product selectivity depends on the species involved in the reduction of CO_2 in ionic liquids. The presence of single ionic liquid CO_2 yields of CO, whereas the presence of protons (acid H[NTf2]) allows production of HCOOH.

Electrooxidation of CO (Chapter 7) has been made for two reasons: one of them is the fact that CO is a reduction product / or intermediate in CO_2 reduction, while the second refers to the fact that the adsorption of CO is the critical stage (surface active poisoning) in many oxidation reactions encountered in the synthesis and fuel cells.

It has been shown that CO electrooxidation is a sensitive process to the electrode surface and the electrocatalytic activity of the electrodes follows the order below:

Pt (110) > Pt (111) > Pt (100)

The nature of the anion of the ionic liquid has a significant effect on the process as it competes electrooxidation reaction of CO at the active surface of the catalyst, controlling overpotential necessary to complete the process of CO_{ad} electrooxidation.

For electrochemical reduction of CO_2 into the reactor media filters were first carried out cyclic voltammetry experiments analyzing the behavior of the Pb electrode in the alkaline carbonate and sodium sulphate (Chapter 8) .

Experiments conducted in solutions of Na_2CO_3 in the presence of dissolved CO_2 have a peak at - 1.6V potential which is attributed to CO_2 reduction. Using a less reactive electrolyte as Na_2SO_4 allowed evaluation of the influence of CO_2 on the process. In Na_2SO_4 solution deaerated with Ar only HER has been identified.

The influence of pH is particularly important for CDER on Pb electrode. The use of sodium carbonate as an electrolyte solution increased the pH. The current`s best yields were obtained for the electrolyte solutions having a pH that is close to 7, for instance Na_2SO_4 (62 %), Na_2SO_4 +Na_2CO_3 (58 %) .

Following lengthy electrolysis in electrochemical reactor (Chapter 9) electrochemical reduction of CO_2 on Pb electrode was carried out at different current densities and different electrolyte solutions. Reduction product obtained was $HCOO^-$.

Measurements have shown that the useful product of CDER depends on the type of electrolyte and pH . The higher current efficiency $HCOO^-$ was 39% and was obtained in sodium sulfate solution. Lengthy electrosynthesis revealed that a higher current efficiency is favored by operating at low current density in this case 5mA/cm^2. The current efficiency decreased with time in the course of the electrolysis so that the highest current efficiency for HCOOH was 39 % for 30 minutes of electrolysis, and after 120 minutes it decreased to 10 %." Desactivation" of the cathode in time may be due to the formation of organometallic complex electrode.

Based on the data presented in Chapter 9 and in the literature it was assessed the CE mass balance (see chapter 10). Calculations based on mass balance equations have been carried out for hourly output of 68 kg of sodium formate.

Relatively to specific consumptions obtained it can be said that they are comparable to those reported in the literature. Superior value to literature data on the specific energy consumption for sodium formate can be explained by the superior performance achieved by RE used , that is a short distance interpolation (low ohmic drop) but also by good electrical conductivity of the sodium sulfate solution relative to the carbonate solution used in other studies.

In the future, additional measurements will be carried out in pilot plant scale in order to verify: (i) the practical possibility to obtain solution of concentrated sodium formate , (ii) the ability to operate the current density per unit volume of larger reactor, using porous or volume electrode. Developing a protocol for tracking sodium formate concentration is also very necessary.

LIST OF PUBLICATIONS

1. **F. A. Hanc-Scherer**, C. M. Sánchez-Sánchez, P. Ilea, E. Herrero, *Surface-Sensitive Electrooxidation of Carbon Monoxide in Room Temperature Ionic Liquids*, ACS Catalysis, **2013**, 3, 2935−2938.
2. **F. A. Hanc-Scherer**, P. Ilea, *Electrochemical Reduction of CO2 on lead Electrode. I. Cyclic Voltammetry and Long Time Electrosynthesis Studies*, Studia UBB Chemia, **2013**, 3, 75-84.
3. **F. A. Hanc-Scherer**, A. Nicoară, C*oupled voltammetric and electrogravimetic investigation of copper behavior in carbonate-bicarbonate solutions*, Studia UBB Chemia, **2013**, 4, 183-191.

LIST OF CONFERENCES

1. **F. A. Hanc**, P. Ilea, *Electrochemical reduction of CO2 I. Cyclic voltammetry (CV) studies at a copper electrode*, ***Poster***, „ The International Conference ENVIRONMENT & PROGRESS Environment-Research, Protection and Management, Cluj-Napoca, **2011.**
2. **F. A. Hanc**, A. Nicoară, P. Ilea, *Electrochemical investigation of reduction* CO_2 *kinetics on copper electrode*, ***Poster***, Third Regional Symposium on Electrochemistry South-East Europe RSE-SEE3, Bucharest, **2012.**
3. **F. A. Hanc-scherer**, C. M. Sánchez sánchez, E. Herrero rodríguez, P. Ilea, *Electrochemical CO2 reduction in room temperature ionic liquids (RTILs) Preliminary studies*, ***Prezentare orală,*** 18th Romanian lnternational Conference on Chemistry and Chemical Engineering, Sinaia, **2013.**