

## REFERENCES

- Project RP114-2 Annual Report no. EM-1328, January 1980, Power Systems Division of United Technologies Corporation.
- Project RP114-1 Final Report no. EM-335, October 1976, Power Systems Division of United Technologies Corporation.
- Project RP239-4, Report no. AP1543, Fluor Engineers and Constructors.
- Project 8984 Final Status Report, Vol. II, Task II., September 1977, Institute of Gas Technology.
- C. E. Vallet and J. Braunstein, *This Journal*, **126**, 527 (1979).
- C. E. Baumgartner, *ibid.*, **131**, 1850 (1984).
- Project RP114-2 Annual Report, EPRI EM-956, December 1978, United Technologies Corporation.
- Project RP-1085-2 Interim Report, July 1979, Institute of Gas Technology.
- Project RP1085-2 Interim Report, February 1981, Institute of Gas Technology.
- (a) DOE Contract no. DE-AC21-83MC20212, Final Report, May 1986, Institute of Gas Technology; (b) Interim Report, October 1983; (c) Interim Report, July 1985.
- H. S. Huang ANL-84-38, Argonne National Laboratory, Argonne, IL (1984).
- V. M. Vogel and S. W. Smith, *This Journal*, **129**, 1441 (1982).
- D. Townley, J. Winnick, and H. S. Huang, *ibid.*, **127**, 1104 (1980).
- M. Kesten and H. G. Feller, *Electrochim. Acta.*, **16**, 763 (1971).
- M. Kesten, *et al.*, *This Journal*, **119**, 722 (1972).
- R. L. Cowan and R. W. Staehle, *ibid.*, **118**, 557 (1971).
- G. Enterlein and H. G. Feller, *Zashch. Met.*, **65**, 697 (1974).
- I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin (1973).
- I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances—Supplement," Springer-Verlag, Berlin (1977).
- T. Rosenquist, *J. Iron Steel Inst., London*, **176**, 37 (1954).
- J. R. Rostrup-Nielsen, *J. Catal.*, **11**, 220 (1968).
- I. Alstrup, J. R. Rostrup-Nielsen, and S. Roen, *Appl. Catal.*, **1**, 303 (1981).
- J. G. McCarty and H. Wise, *J. Chem. Phys.*, **72**, 6332 (1980).
- B. G. Ong, T. A. Lin, and D. M. Mason, in "Electrode Materials and Processes for Energy Conversion and Storage," Vol. 87-12, S. Srinivasan, S. Wagner, and H. Wroblowa, Editors, p. 295, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1987).
- G. Wilemski, T. Wolf, D. Bloomfield, M. C. Finson, E. R. Pugh, and K. L. Wray, DOE Contract no. DE-AC-03-79ET 11322, Final Report, Physical Sciences, Inc., August (1979).
- (a) J. J. Bikerman, "Physical Surfaces," p. 97, Academic Press, New York, (1970); (b) G. A. Samorjai, "Principles of Surface Chemistry," p. 64, Prentice-Hall, Englewood Cliffs, NJ (1972); (c) R. Defay and I. Prigogine, "Surface Tension and Adsorption," p. 166 Wiley, New York (1966).
- R. Avegard and D. A. Haydon "Introduction to the Principles of Surface Chemistry," Cambridge, London (1973).
- P. G. P. Ang and A. F. Sammells, *This Journal*, **127**, 1287 (1980).
- A. F. Sammells, S. B. Nicholson, and P. G. P. Ang, *ibid.*, **127**, 350 (1980).
- T. Wolf and G. Wilemski, *ibid.*, **130**, 48 (1980).
- Energy Research Corporation, DOE/ET/11304-19 (1980).

## Electrochemical and Surface Studies of Carbon Dioxide Reduction to Methane and Ethylene at Copper Electrodes in Aqueous Solutions

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### ABSTRACT

The electrochemical reduction of CO<sub>2</sub> to CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> in aqueous alkaline solutions at Cu electrodes was studied under potentiostatic conditions at -2.00V vs. SCE. The current at the Cu electrodes and the rate of hydrocarbon formation were monitored as a function of time over a temperature range from 0 to 48°C. Solutions of formate, formaldehyde, and methanol, possible intermediates in the reduction process, were also electrolyzed. Surface analyses (XPS and AES) were also performed on the Cu electrodes following electrolysis to identify surface intermediates. In addition to hydrocarbon formation, a poisoning process occurred, causing a deposit of a black film on the surface of the Cu cathode. XPS and AES studies indicated that the black film was graphitic carbon, probably the result of a side reaction, the reduction of CO<sub>2</sub> through formate to graphite. A tentative reaction mechanism for CO<sub>2</sub> reduction, based upon the data here and those of previous investigators, involving the reaction path CO<sub>2</sub> → CO → surface-bound formyl (Cu-HCO) → surface-bound methylene (Cu=CH<sub>2</sub>) → hydrocarbon products, is proposed.

We report here electrochemical and surface studies on the electroreduction of CO<sub>2</sub> to CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> at copper foil electrodes in aqueous solutions. The conversion of CO<sub>2</sub> to hydrocarbon products is an attractive process for energy storage (CH<sub>4</sub>) and as an alternative to petrochemical feedstocks (C<sub>2</sub>H<sub>4</sub>). The development of this process, which may be important when the world's fossil fuel reserves are depleted, has been the subject of many investigations. For example, the catalytic methanation of CO<sub>2</sub> by transition

metals (1) and their complexes (2) has been well studied. More recently, efforts have been directed to the photoreduction (3) and electrochemical reduction (4, 5) of CO<sub>2</sub> to organic fuels. From studies of heterogeneous gas phase catalytic processes, ruthenium was chosen as the electrode material for the electrochemical reduction of CO<sub>2</sub> to hydrocarbon products with high efficiency. Copper metal, on the other hand, is completely inactive as a heterogeneous catalyst for the gas phase hydrogenation of CO, CO<sub>2</sub>, or CO/CO<sub>2</sub> mixtures to CH<sub>3</sub>OH or CH<sub>4</sub> (6, 7), although it is used as a promoter in alloy catalysts (1-3, 6-8). The promoting properties of copper are attributed to participation of a partially oxidized species (8) or to a diluent effect (7). Although

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early electrochemical studies indicated that copper was inactive for CO<sub>2</sub> reduction to organic fuels, producing only formate (9), Hori *et al.* (10) reported the electrochemical reduction of CO<sub>2</sub> to CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> from aqueous solutions at copper foil electrodes with high current efficiencies. This initial report has been followed by additional studies (11-15). The optimized faradaic efficiency of hydrocarbon production was found to be nearly 100% for short periods of time at a current density of 8.3 mA cm<sup>-2</sup> (13). The use of Cu/Nafion electrodes (solid polymer electrolyte structures) for the gas phase electrochemical reduction was also demonstrated (15, 16). However, the reaction mechanism of the CO<sub>2</sub> to hydrocarbon process has not been elucidated. Previous studies of the reduction of CO<sub>2</sub> at Cu foil electrodes in aqueous carbonate solutions have shown that:

1. The major hydrocarbon products are CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, while the minor products are CO and HCOOH, with no detectable formation of CH<sub>3</sub>OH or H<sub>2</sub>CO (10);

2. the potential required for the onset of CH<sub>4</sub> production is near -1.6V *vs.* SCE, while optimal faradaic efficiencies are found at potentials near -2.0V *vs.* SCE (14);

3. C<sub>2</sub>H<sub>4</sub> production increases with increasing temperature, while CH<sub>4</sub> production and overall hydrocarbon formation efficiencies decrease with increasing temperature (10, 14, 15); and

4. CO can also be reduced at Cu electrodes with results similar to those obtained with CO<sub>2</sub> as a substrate (14, 17).

The purpose of this study was to investigate the possible reaction mechanisms of this process.

### Experimental

High-purity copper foils (99.999%, Aesar, Incorporated, Seabrook, New Hampshire) were degreased by boiling for 1h in CH<sub>2</sub>Cl<sub>2</sub> (certified ACS grade, Fisher Scientific, Incorporated, Fair Lawn, New Jersey), 1h in absolute EtOH (Midwest Grain Products, Perkin, Illinois), and then rinsed with copious amounts of milliQ water (Continental Water Systems, El Paso, Texas). Prior to electrolysis, the foils were immersed in 1.0M HCl to remove any oxidized Cu species (14) and rinsed again with milliQ water. Electrolyses were carried out in a two-compartment cell. The working compartment held the Cu electrode (1 × 1 cm) and approximately 25 ml of solution and was separated from the counterelectrode compartment by a fine porosity glass frit. A platinum flag (2.5 × 2.5 cm) was utilized as an auxiliary electrode in the counter compartment. A saturated calomel electrode (SCE) was used as the reference and was separated from the working solution by a glass frit and an agar-filled (KCl saturated) isolation chamber.

Carbonate solutions were prepared from KHCO<sub>3</sub> (ACS reagent grade, MCB Manufacturing Chemists, Incorporated, Cincinnati, Ohio) and milliQ water. Before each electrolysis, the fresh carbonate solutions were purged with and saturated by vigorous bubbling with CO<sub>2</sub> for 30 min. Gaseous CO<sub>2</sub> was obtained from the sublimation of Dry Ice and humidified by passing through 0.5M KHCO<sub>3</sub> before introduction to the working chamber of the cell. A gas dispersion tube functioned as the gas inlet to the cell and was positioned to allow the CO<sub>2</sub> to impinge directly on to the Cu foil cathode. Effluent gases from this continuous flow system were collected in 25 ml aliquots with inverted test tubes filled with, and immersed in, water. Analyses of the hydrocarbon products were performed on a Varian Model 1860 gas chromatograph (Varian Associates, Palo Alto, California) equipped with a flame ionization detector. The chromatographic column, a 6 ft × 1/8 in. od stainless-steel column packed with 80/100 mesh Porapak Q (Alltech Associates, Incorporated, Deerfield, Illinois), was employed under isothermal conditions at 50°C with a He carrier gas flow of 25 ml/min. Quantitation of products was performed by a Hewlett-Packard Model 3392A integrator (Palo Alto, California) on the basis of peak areas with duplicate injections. Accuracy of the assay was checked daily, before and after each experimental run, with a standard mixture of methane, ethylene, and ethane (50, 100, and 50 ppm, respectively) in humidified CO<sub>2</sub>. Sample deviation was less than 5%. Analyses for solution products MeOH and H<sub>2</sub>CO in the bicarbonate buffers were performed with the same

chromatographic column under isothermal conditions at 125°C, while trapping agent (allyl alcohol) and product (cyclopropane methanol) studies were run at 200°C.

XPS spectra were taken on a VG ESCALAB 5 spectrometer, utilizing a Mg anode dissipating 270W. The pass energy of the analyzer was 20 eV in all experiments. Auger (AES) spectra were recorded with the same apparatus with an electron beam energy of 3 keV.

All electrolyses were performed with an EG&G Princeton Applied Research (PAR, Princeton, New Jersey) Model 173 potentiostat/galvanostat. KOH (certified ACS, Fisher Scientific), MeOH (absolute, J. T. Baker Chemical Company, Phillipsburg, New Jersey), formaldehyde (37% w/w solution with 10-15% MeOH as preservative, certified ACS, Fisher Scientific), and formic acid (88%, certified ACS, Fisher Scientific) were used without further purification.

### Results

*Current efficiency for methane and ethylene formation.*—Electrolyses were performed under potentiostatic conditions, while the current and the product concentration in cell effluent were monitored as a function of time. Current efficiencies for hydrocarbon production (CE) from CO<sub>2</sub> reduction were calculated on the basis of 8 equiv. consumed per mole methane formed, 12 equiv. per mole ethylene formed, 14 equiv. per mole ethane formed, and the ideal gas volume of 22.4 liter/mol. Figure 1 illustrates typical behavior of current and current efficiency *vs.* time for a Cu foil electrode held at a potential of -2.00V *vs.* SCE in a 0°C solution of 0.5M KHCO<sub>3</sub>, with a CO<sub>2</sub> flow rate of 45 ml/min. The time profile of total hydrocarbon production showed a steady rise from the start of the electrolysis to a peak after approximately 20 min. This was followed by a rapid decay to nearly zero after 120 min. The hydrocarbon product in

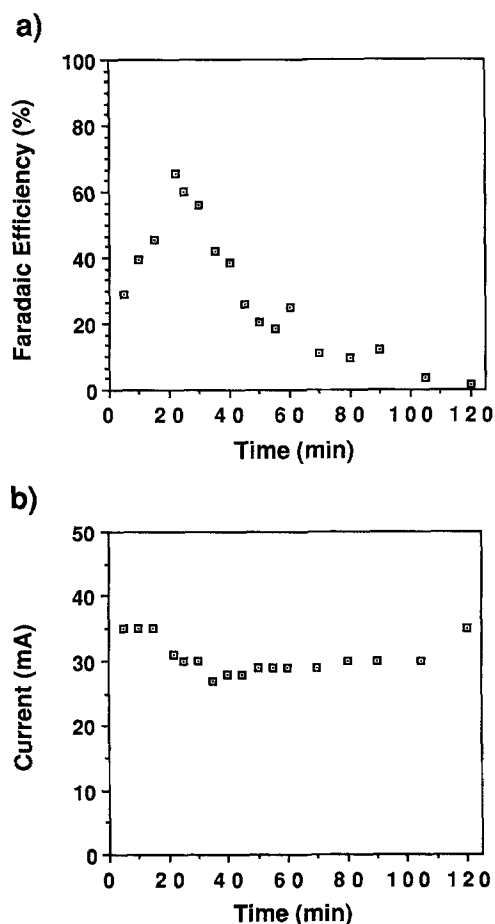


Fig. 1. Electrolysis results for CO<sub>2</sub> reduction at a Cu foil electrode in 0.5M KHCO<sub>3</sub>. Area of electrode = 2 cm<sup>2</sup>, electrode potential = -2.00V *vs.* SCE, temperature = 0°C, CO<sub>2</sub> flow rate = 45 ml/min: (a) total hydrocarbon faradaic efficiency *vs.* time and (b) current *vs.* time.

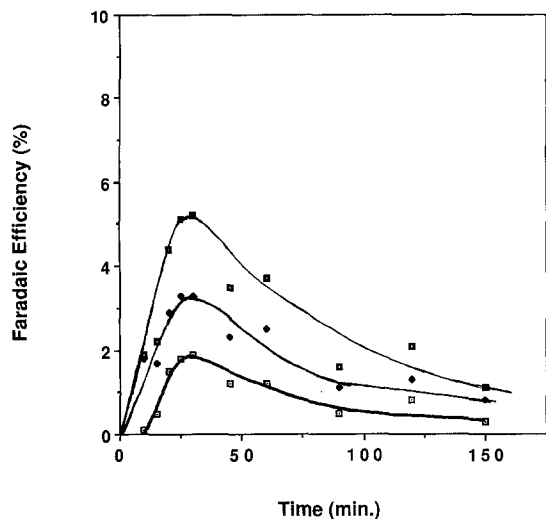


Fig. 2. Current efficiency vs. time for  $\text{CO}_2$  electrolysis at a Cu foil electrode in  $0.5\text{M KHCO}_3$  at  $26^\circ\text{C}$  (conditions as in Fig. 1):  $\square$ , methane;  $\blacklozenge$ , ethylene;  $\square$ , total.

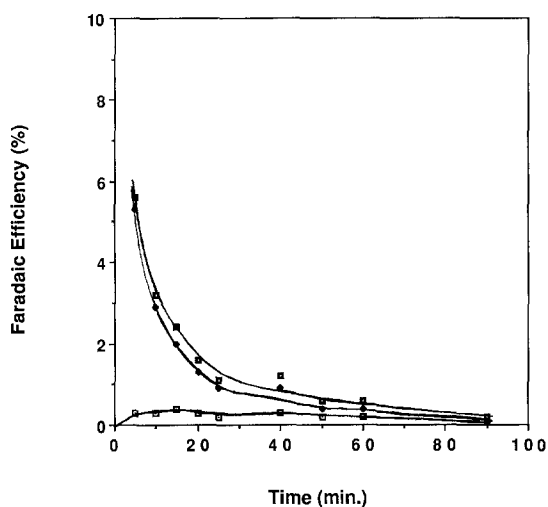


Fig. 3. Current efficiency vs. time for  $\text{CO}_2$  electrolysis at a Cu foil electrode in  $0.5\text{M KHCO}_3$  at  $48^\circ\text{C}$  (conditions as in Fig. 1):  $\square$ , methane;  $\blacklozenge$ , ethylene;  $\square$ , total.

the cell effluent was mostly methane, with little ethylene observed. Often, at the end of the electrolysis, the foil electrode appeared darker, with a thin black coating along the edges of the foil.

An increase in the temperature to  $26^\circ\text{C}$  did not change the shape of the current efficiency vs. time behavior, as shown in Fig. 2. The CEs were about a tenth of those observed at  $0^\circ$ , but the current at  $26^\circ$  was 10 times greater than that at  $0^\circ$ , so that the overall rate of hydrocarbon formation was about the same. Ethylene was produced in significantly greater amounts than at  $0^\circ$ , comprising ca. 63% of the total hydrocarbon CE, while methane formation was reduced, compared to that at  $0^\circ$ . At  $48^\circ$ , the behavior of the CE vs. time did not show the early period of increasing efficiency to a peak value (Fig. 3). Only a rapid decay of efficiency from the beginning of the electrolysis was observed. The currents at  $48^\circ$  were ca. 1.5 times those at  $26^\circ$  (15 times those at  $0^\circ$ ). The hydrocarbon product distribution shifted almost completely to ethylene, with little methane formation observed.

At  $0^\circ$  and  $26^\circ$ , the peak of CE was reached after 20–25 min of electrolysis. At  $0^\circ$ , the peak CE for  $\text{CH}_4$  production was over 60%, corresponding to a rate of  $4.3 \times 10^{-5} \text{ mol h}^{-1} \text{ cm}^{-2}$  (a methane partial current density of  $9.3 \text{ mA cm}^{-2}$ ). At  $26^\circ$ , the peak CE was 1.9 and 3.3% for  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ , respectively, ( $2.5 \times 10^{-5} \text{ mol h}^{-1} \text{ cm}^{-2}$  methane, and  $2.9 \times 10^{-5} \text{ mol h}^{-1} \text{ cm}^{-2}$  ethylene). At  $48^\circ$ , the CE was 0.3 and 5.3% for

methane and ethylene, respectively, ( $2.9 \times 10^{-6} \text{ mol h}^{-1} \text{ cm}^{-2}$  methane and  $3.5 \times 10^{-5} \text{ mol h}^{-1} \text{ cm}^{-2}$  ethylene). These rates are comparable to those reported elsewhere under galvanostatic conditions (10–14).

**XPS analysis.**—The x-ray photoelectron (XPS) spectra of C(1s) on a Cu electrode before and after use in a  $\text{CO}_2$  electrolysis are shown in Fig. 4. The “active” electrode is a Cu foil which had been cleaned and had undergone 10 min of  $\text{CO}_2$  electrolysis at  $-2.00\text{V vs. SCE}$  at  $0^\circ\text{C}$  in  $0.5\text{M KHCO}_3$  solution. This active electrode was confirmed, by a gas chromatographic analysis of cell effluent, to be actively reducing  $\text{CO}_2$  to  $\text{CH}_4$ . The control foil was also cleaned and placed in the  $0.5\text{M KHCO}_3$  solution at  $0^\circ$  for 10 min, but no potential was applied. The rest potential of the Cu foil in the carbonate buffer at  $0^\circ$  was ca.  $-0.1\text{V vs. SCE}$ . The XPS spectrum of the control electrode only showed a transition centered at 284.5 eV. The spectrum of the active electrode contained an additional peak at 287 eV, which appears as a shoulder on the 284.5 eV peak. This same behavior was observed in two separate trials under the same conditions. We ascribe the shoulder to an intermediate in the electrolysis, as discussed below.

**Electrolysis of possible intermediates.**—The electrolysis of CO, formic acid, formaldehyde, and methanol solutions was also investigated, since they are possible reaction intermediates in the reduction of  $\text{CO}_2$  to methane. As previously reported (17), CO was reduced to  $\text{CH}_4$  at  $-2.00\text{V vs. SCE}$  in  $0.5\text{M K}_2\text{HPO}_4$  ( $\text{pH} = 9.4$ ) at  $0^\circ$ . The CE vs. time behavior is shown in Fig. 5. The peak of CE corresponded to  $2.0 \times 10^{-5} \text{ mol h}^{-1} \text{ cm}^{-2}$  ( $3.2 \text{ mA}$  partial methane current density). Electrolyses were attempted with 88%  $\text{HCOOH}$  and 37%  $\text{CH}_2\text{O}$  in aqueous solutions, and neat  $\text{CH}_3\text{OH}$ , with  $1.0\text{M KOH}$  as supporting electrolyte at  $0^\circ$  and a potential of  $-2.00\text{V vs. SCE}$ . The CE vs. time behavior is shown in Fig. 6. The electrolysis of a formic acid solution yielded little methane. However, the time profile of methane production was very similar to that observed previously for  $\text{CO}_2$  electrolysis. At the end of the formate electrolysis, a black coating completely covered the surface of the copper foil. This black coating was analyzed by XPS and AES; its spectra are shown in Fig. 7. The XPS measurement shows a transition centered at 283 eV. Figure 7 illustrates the Auger line shape of the carbon (KLL) on the electrode surface. The electrolytic reduction of formaldehyde proceeded at much lower currents than those observed with  $\text{CO}_2$  as substrate, and lower faradaic efficiency. The time profile of methane production showed a slow rise to a

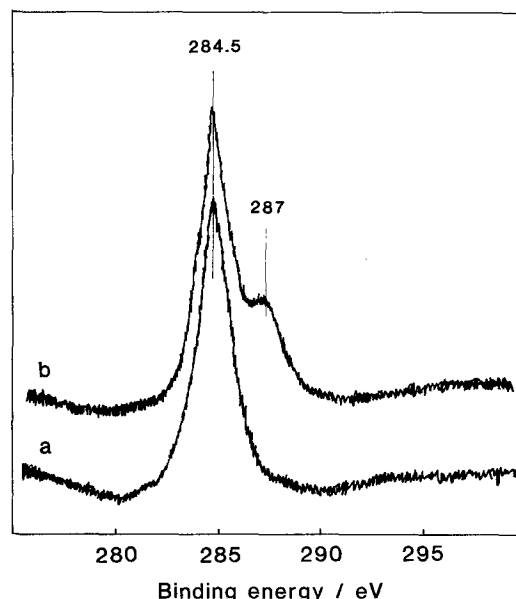


Fig. 4. XPS spectra of Cu cathodes: (a) black film on Cu cathode after electrolysis of a  $1.0\text{M KOH}$  in  $88\% \text{HCOOH}$  solution at  $0^\circ\text{C}$  ( $273 \text{ K}$ ) and (b) a control electrode that had been cleaned and placed in a cold bicarbonate buffer, not a potential was applied.

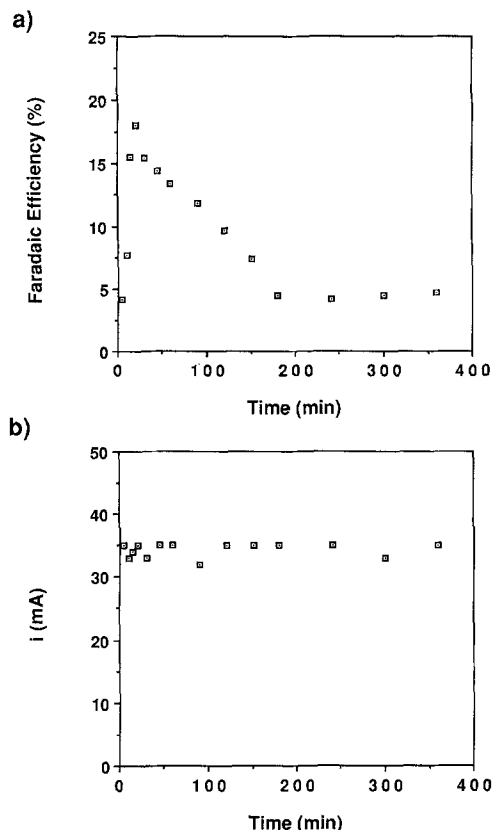
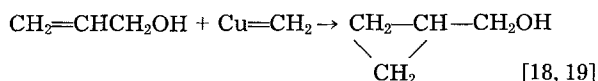


Fig. 5. Current efficiency vs. time for CO electrolysis at a Cu foil electrode in 0.5M  $K_2HPO_4$  (other conditions as in Fig. 1).

steady-state value after *ca.* 75 min. This rate of hydrocarbon production was maintained for over 5h of electrolysis. After the electrolysis, the Cu foil was as bright and shiny as before the electrolysis. With methanol as a substrate, no methane was detected in the cell effluent throughout the duration of a 90 min electrolysis. The foil also appeared bright and shiny at the end of the methanol electrolysis.

**Trapping experiments.**—As described below, a possible reaction intermediate is a carbenoid species, represented as  $Cu=CH_2$ . We attempted to obtain evidence for this species by trapping it with allyl alcohol ( $CH_2=CH-CH_2OH$ ) following the strategy of Ward and Eckerdt (18), who trapped alkyl intermediates during studies of the Fischer-Tropsch synthesis. Copper-methylene species are soft electrophiles, unable to insert in carbon-hydrogen bonds, but capable of addition to olefins (18, 19). Allyl alcohol was chosen as the scavenging agent, since the result of MeOH electrolysis suggested that the alcohol functionality would not poison the cathode surface, nor undergo degradation via side reactions at the electrode. We hoped that the copper-bound methylene would add across the olefin to form the cyclopropane derivative



From the detection limits for the cyclopropane methanol GC method, we calculated that a minimum trapping efficiency of 1% was necessary to observe the products of trapped intermediate. That is, we would expect to detect cyclopropane methanol if the agent (allyl alcohol) would scavenge 1% of the total methylene produced during an electrolysis. However, we were unable to detect cyclopropane methanol in the gaseous cell effluent, or in solution after 1h electrolysis of  $CO_2$  in the presence of 10% (v/v) allyl alcohol in 0.5M  $KHCO_3$ .

**Discussion.**—The overall reaction path from  $CO_2$  to  $CH_4$  and  $C_2H_4$  is clearly a complicated one involving electron transfers, protonations, hydrogen atom or hydride additions, C—O bond cleavages, and numerous intermediates.

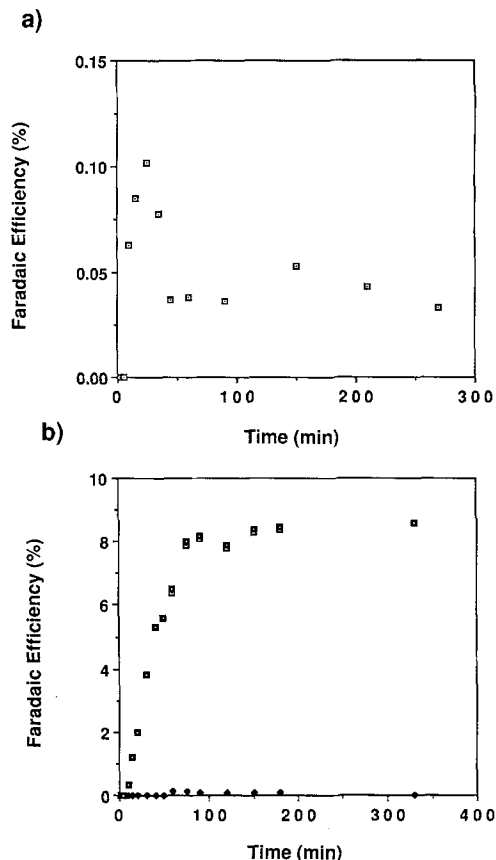


Fig. 6. (a) Faradaic efficiency vs. time for the electrolysis of 88% formate with 1.0M KOH as electrolyte. Potential =  $-2.00V$  vs. SCE, temperature =  $0^\circ C$ ,  $N_2$  flow rate = 45 ml/min. (b) Faradaic efficiency vs. time for electrolysis of 37% formaldehyde with 1.0M KOH as electrolyte. Same conditions as above:  $\square$  methane,  $\blacklozenge$  ethylene,  $\circ$  total.

Based on the results obtained here and by analogy with previous experiments, we can only attempt to explain the poisoning of the electrode and give a tentative overall mechanism for the reaction. We propose the mechanism of Scheme I.

The hydrocarbons are generated along with  $H_2$  with an essentially constant current for the sum of the reactions as a function of time. The rate of hydrocarbon production, however, shows a time dependence (Fig. 1 and 2) characterized by an induction period, a growth to a maximum rate, and then a decay. Such a pattern suggests the buildup of intermediates in the hydrocarbon generation reaction

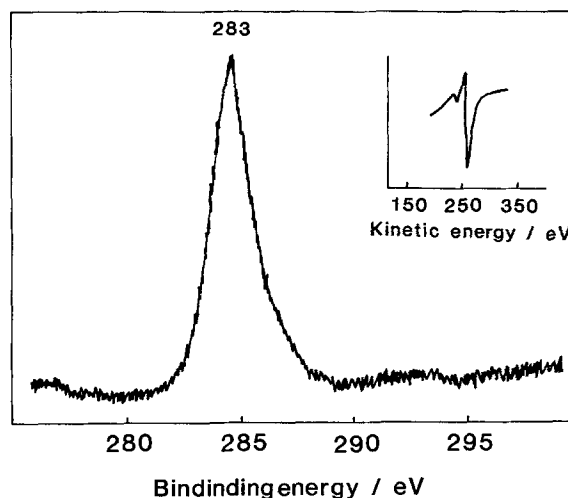


Fig. 7. XPS spectrum of a Cu cathode after electrolysis in 88% formic acid with 1.0M KOH as electrolyte. Inset: AES C(1s) line shape.



## REFERENCES

- G. A. Mills and F. W. Steffgen, *Catal. Rev.*, **8**, 159 (1973).
- A. Behr, in "Catalysis in C<sub>1</sub> Chemistry," W. Keim, Editor, p. 169. D. Reidel Publishing Co., Dordrecht, Holland (1983).
- I. Willner, R. Maidan, D. Mandler, H. Dürr, G. Dörr, and K. Zengerle, *J. Am. Chem. Soc.*, **109**, 6080 (1987), and references cited therein.
- (a) K. W. Frese and S. Leach, *This Journal*, **132**, 259 (1985); (b) D. P. Summers and K. W. Frese, *Langmuir*, **4**, 51 (1988).
- S. Kapusta and N. Hackerman, *This Journal*, **130**, 607 (1983).
- L. E. Cratty and W. W. Russell, *J. Am. Chem. Soc.*, **80**, 767 (1958).
- M. Araki and V. Ponc, *J. Catal.*, **44**, 439 (1976).
- K. Klier, V. Chatikavanij, R. G. Herman, and G. W. Simmons, *ibid.*, **74**, 343 (1982).
- P. G. Russell, N. Kovak, S. Srinivasan, and M. Steinberg, *This Journal*, **124**, 1329 (1977).
- Y. Hori, K. Kikuchi, and S. Suzuki, *Chem. Lett.*, 1695 (1985).
- Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, *ibid.*, 897 (1986).
- R. L. Cook, R. C. MacDuff, and A. F. Sammells, *This Journal*, **134**, 1873 (1987).
- R. L. Cook, R. C. MacDuff, and A. F. Sammells, *ibid.*, **134**, 2375 (1987).
- K. W. Frese, D. P. Summers, and J. J. Kim, Private communication.
- D. W. DeWulf and A. J. Bard, *Catal. Lett.*, **1**, 73 (1988).
- R. L. Cook, R. C. MacDuff, and A. F. Sammells, *This Journal*, **135**, 1320 (1988); A. F. Sammells, R. L. Cook, and B. W. Wessels, Private communication.
- Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, *J. Am. Chem. Soc.*, **109**, 5022 (1987).
- C. J. Ward and J. G. Eckerdt, *J. Catal.*, **86**, 239 (1984) and references cited therein.
- W. Kirmse, "Carbene Chemistry," 2nd ed., Academic Press, New York (1971).
- "Solubilities of Inorganic and Organic Compounds," Vol. 1, H. Stephen and T. Stephen, Editors, pp. 364-366, MacMillan Co., New York (1963).
- R. A. Hadden, H. D. Vandervell, K. C. Waugh, and G. Webb, *Catal. Lett.*, **1**, 27 (1988).
- G. Henrici-Olivé and S. Olivé, *Angew. Chem. Int. Ed. Engl.*, **15**, 136 (1976).
- W. A. Herrmann, *ibid.*, **21**, 117 (1982).
- J. Saussey, J.-C. LaValley, J. Lamotte, and T. Rais, *J. Chem. Soc., Chem. Comm.*, 278 (1982).
- U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **2**, 70 (1970).
- (a) D. P. Summers and K. W. Frese, *Langmuir*, **4**, 51 (1988); (b) K. W. Frese and S. Leach, *This Journal*, **132**, 259 (1985).
- L. Ramqvist, K. Hamrin, G. Johansson, and A. Fahlmann, *J. Phys. Chem. Solids*, **30**, 1835 (1969).
- S. Akhter and J. M. White, *Surf. Sci.*, **180**, 19 (1987).
- A. J. Hubert, in "Catalysis in C<sub>1</sub> Chemistry," *op. cit.*, p. 263.
- (a) R. C. Brady III and R. Pettit, *J. Am. Chem. Soc.*, **102**, 6181 (1980); (b) R. C. Brady III and R. Pettit, *ibid.*, **103**, 1287 (1981).
- F. Greuter and E. W. Plummer, *Solid State Commun.*, **48**, 37 (1983).

# Thermoelectric Theory of Electronic Conductors

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## ABSTRACT

A new treatment of thermoelectric effects in electronic conductors is proposed. The treatment uses only the first and second laws of thermodynamics together with certain laws of local energy and heat production. It is shown how Thomson's relations can be derived without further assumptions, *i.e.*, Onsager reciprocal relations. A simple thermodynamic analogue of the system is presented to emphasize essential points.

The main objective of our work on nonisothermal systems is to develop a general theory for thermoelectricity. By a general theory we mean a theory derived from the laws of delocalized conservation of mass and energy in a system. Final equations shall imply the time dependency of all variables. No use shall be made of the concept of entropy production in the sense of irreversible thermodynamics or of Onsager reciprocal relations. Thus we think the method shall be easy to apply in practice.

The conservation laws for mass and energy have been used before to derive the EMF of isothermal systems (1). By extending the application to nonisothermal cases, we may introduce complications stepwise, *i.e.*, the electronic conductor should be treated before the electrochemical cell. Thus the analyses of the two cases follow consecutively in the present and next paper (2).

For electronic conductors, the law of local mass conservation is trivially fulfilled, and we need only consider the conservation of energy to calculate electric potential differences (EMFs). In the thermocell, it is necessary to deal with delocalized mass conservation, too, since charge transfer leads to mass transfer.

The physical basis and the method of derivation is the main message of both works. Specifically it will be shown

in the present paper that the first and second relations of Thomson are direct results from the fundamental laws and the derivation.

## Theory

*System design.*—A specific example is chosen to illustrate the derivation. The system is treated in several textbooks [see *e.g.*, Ref. (3-6)]. Consider the system shown in Fig. 1. A wire of cross section  $A$  and length  $l$  consists of two different components (conductors). A piece of component 2 is built in between two pieces of component 1, the connections are at  $x = x_{12}$  and  $x = x_{21}$ . Assume for  $t = 0$  that temperature,  $T$ , is constant along the wire from  $x = 0$  to  $x = l$ . At the two ends  $x = 0$  and  $x = l$  we apply electric work.

*Delocalized energy conservation.*—In our test experiment a small charge is passed through the wire. Mass changes do not occur. Conservation of energy in the total system and surroundings is expressed by the first law of thermodynamics

$$(dU/dt) - (dQ/dt) = dW_{el}/dt \\ = -EI + RI^2 = -EjA + R(jA)^2 \quad [1a]$$

$(dU/dt)$  is the time change of the internal energy in  $\text{Js}^{-1}$ ,  $(dQ/dt)$  is a flux, the total heat received per unit time by the system in  $\text{Js}^{-1}$ ,  $dW_{el}/dt$  is the electric work supplied per

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