Office of Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy, under contract DE-AC03-76SF00098.

Manuscript submitted June 1, 1987; revised manuscript received Dec. 18, 1987.

Lawrence Berkeley Laboratory assisted in meeting the publication costs of this article.

REFERENCES

1. P. N. Ross and H. Sokol, *This Journal,* **131,** 1742 (1984).
2. N. Staud and P. N. Ross, *ibid.,* **133,** 1079 (1986).
3. Kirk-Othmer, in "Encyclopedia of Chemical Technology," Vol. 4, Third Ed., pp. 631-66, John Wiley and Sons, New York (1978).
4. A. J. Groszek and G. I. Andrews, "Some Adsorptive Properties of Polar and Basal Plane Sites in Graphite," pp. 156-64, Society of the Chemical Industry, London (1971).
5. J. P. Randin and E. Yeager, *This Journal,* **118,** 711 (1971).
6. *J. Electroanal. Chem.,* **36,** 257 (1972).
7. *ibid.,* **58,** 313 (1975).
8. B. E. Warren, "X-Ray Study of the Graphitization of Carbon Black," Proceedings of the First and Second Conferences on Carbon, pp. 49-58, Waverly Press, Baltimore, MD (1956).
9. G. M. Jenkins, K. Kawamur, and L. L. Ban, *Proc. R. Soc. (London),* **327,** 501 (1972).
10. "Standard Method of Testing Carbon Black—Iodine Adsorption Number," Annual Book of ASTM Standards, Part NO. 37, p. 379 (1982).

Technical Note

Ambient Temperature Gas Phase CO_2 Reduction to Hydrocarbons at Solid Polymer Electrolyte Cells

Ronald L. Cook,* Robert C. MacDuff, and Anthony F. Sammells*

Eltron Research, Incorporated, Aurora, Illinois 60504

The utility of copper as an electrocatalytic site for promoting high rate CO_2 reduction in CO_2 saturated aqueous $KHCO_3$ ($pH \cong 7.5$) to give both CH_4 and C_2H_4, has recently been reported both by ourselves (1, 2) and others (3-5). CO_2 reduction under these experimental conditions was typically found to proceed at $\cong -1.7$V *vs.* SHE. If the initial step in the CO_2 reduction mechanism involves direct chemical reaction between electrochemically generated chemisorbed hydrogen and adsorbed CO_2 at the copper electrode (6), then one might in principle require less cathodic overpotentials to promote CO_2 reduction using more acid electrolytes. Of course in conventional aqueous electrolyte cells what one would observe under such conditions would be a progressive dominance by hydrogen evolution over CO_2 reduction. One strategy to overcome this limitation is the use of solid polymer electrolyte (SPE) cells.

Discussed here is recent work performed in our laboratory on CO_2 reduction at SPE cells processing the general configurations

$$CO_2/Cu/\text{Nafion } 117/aq \cdot K_2SO_4, Pt$$

and

$$CO_2/Cu/\text{Nafion } 117/Pt, N_2(90\%)\ H_2(10\%)$$

The general experimental arrangements used for these cells are shown schematically in Fig. 1. Copper was initially deposited onto one side of a Nafion 117 membrane (0.017 in., H^+ form, equivalent weight 1100) from 0.5*M* K_2SO_4/0.05*M* $CuSO_4$ solution using 1*M* NaOH/1*M* $NaBH_4$ on the other side. Deposition usually took between 15 and 30 min. Following a thorough rinse in distilled water the Cu/Nafion 117 half-cell (1.55 cm^2) was incorporated into the cell shown in Fig. 1A, where aqueous 0.5*M* K_2SO_4 (pH 8.67) was used in the counterelectrode compartment. For the cell shown in Fig. 1B platinum was initially deposited directly onto Nafion 117 from a 0.05*M* H_2PtCl_6 solution, again using 1*M* NaOH/1*M* $NaBH_4$ as a reducing agent on the other side. Copper was then deposited onto the other membrane side using the previously discussed procedure. CO_2 introduced into the cathode chamber was initially

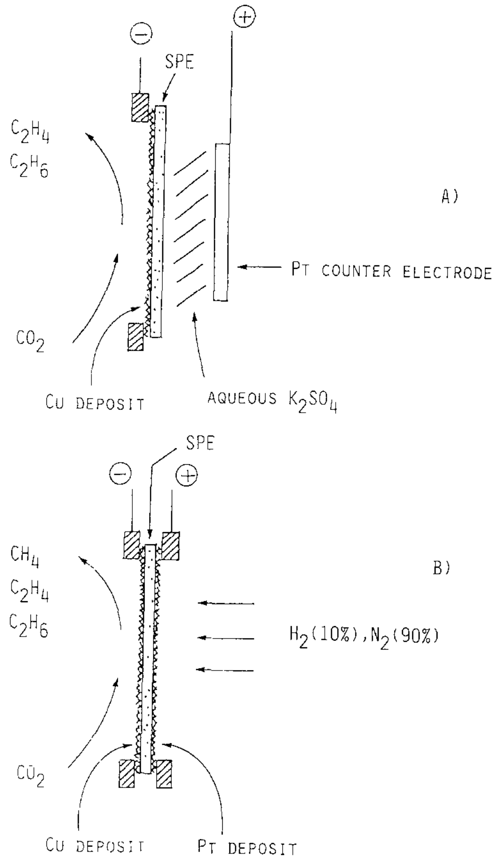

Fig. 1. Schematic solid polymer electrolyte cell arrangement used during this work.

---

* Electrochemical Society Active Member.

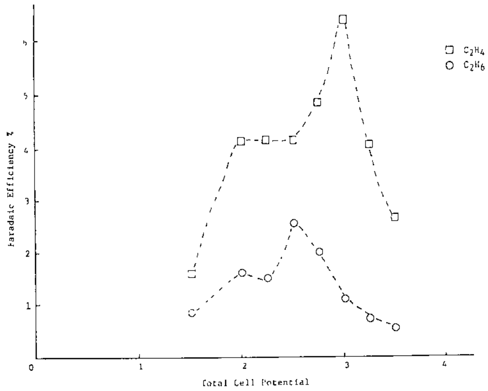

Fig. 2. Faradaic efficiencies for C_2 formation *vs.* applied potential for the cell $CO_2/Cu/Nafion\ 117/K_2SO_4$ (*p*H 8.67)/Pt.

passed through a hydrocarbon trap (gas-dry hydrocarbon trap, Chemical Research Supplies) followed by oxygen removal (Oxy-Trap, Alltech Associates). No hydrocarbons were detected in the CO_2 gas stream after the hydrocarbon trap prior to the SPE cell. Hydrocarbon CO_2 reduction products exiting the cathode chamber were analyzed using a GOW-MAC Model 69-750 FID gas chromatograph using a 6 ft × 1/8 in. stainless steel column packed with 80/100 mesh Carbosphere (Alltech Associates). Constant potential and current electrolyses were performed, controlled by a Stonehart BC 1200 potentiostat/galvanostat. For the experimental arrangement shown in Fig. 1A both C_2H_4 and C_2H_6 were observed as CO_2 reduction products. No CH_4 was observed. For this cell the dependency of faradaic efficiency on total electrolytic cell potential is summarized in Fig. 2, over which electrolysis range the current density varied between 10 and 30 mA/cm^2. This performance was maintained continuously for ≅38h. A significant fraction of the total cell voltage was attributed to both IR losses between the PT counterelectrode in the 0.5*M* K_2SO_4 electrolyte and the SPE, and the oxygen evolution reaction. For preliminary electrolytic cells evaluated using the experimental arrangement shown in Fig. 1B, CH_4, C_2H_4, and C_2H_6 were observed as CO_2 reduction products, although at somewhat lower faradaic yields. This probably reflects however, far from optimum procedures used for preparing the copper working electrode (WE). A significant observation in these cells was that a total cell voltage of only 0.65V was required at 10 mA/cm^2 to promote CO_2 reduction, *i.e.* the Cu WE potential was <0.65V *vs.* SHE. Results are summarized in Table I. We have also promoted CO_2 reduction (at lower yields) at Ni and Rh/SPE interface using analogous cell configurations, to give CH_4. Evidence that CO species (6) are probably intermediates in overall CO_2 reduction is suggested from GC analysis of CO reduction products in the cell.

CO, Cu/Nafion 117/Pt, N_2, H_2(10%)

where CH_4, C_2H_4, and C_2H_6 were observed as CO_2 reduction products (Table II).

Table I. Faradaic efficiencies for the cell $CO_2/Cu/Nafion\ 117/Pt, N_2(90\%)H_2$

Total cell current (mA)	Faradaic efficiency (%)		
	CH_4	C_2H_4	C_2H_6
22.5	t^a	0.34	t^a
30.5	0.071	0.47	0.10
40.4	0.11	1.68	0.22

Flow rate CO_2 = 10 ml min^{-1}, H_2/N_2 = 60 ml min^{-1}.
^{a} t = trace.

Table II. Faradaic efficiencies for the cell CO,Cu/Nafion 117/Pt,N_2H_2(10%)

Total cell current (mA)	Time (min)	Faradaic efficiency (%)		
		CH_4	C_2H_4	C_2H_6
20	15	0.1	2.0	0.17
30	30	0.38	0.13	0.074
40	45	0.39	0.048	—
50	60	0.52	0.051	—
60	75	2.6	—	—

Clearly much work remains before conditions for achieving optimum Cu/SPE interface are identified where efficient high rate CO_2 reduction may be promoted at low cell voltages. However, this brief communication illustrates for the first time that CO_2 reduction can be electrochemically promoted in the gas phase to hydrocarbons at ambient temperatures using an SPE cell, under experimental conditions compatible for eventually achieving practical electrolytic cell voltages.

Acknowledgment

Funding by the Gas Research Institute under Contract no. 5082-260-0671 is gratefully acknowledged.

Manuscript submitted Oct. 7, 1987; revised manuscript received Dec. 17, 1987.

Eltron Research, Incorporated assisted in meeting the publication costs of this article.

REFERENCES

1. R. L. Cook, R. C. MacDuff, and A. F. Sammells, *This Journal*, **134,** 1873 (1987).
2. R. L. Cook, R. C. MacDuff, and A. F. Sammells, *ibid.*, **134,** 2375 (1987).
3. Y. Hori and S. Suzuki, *Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai*, **48,** 213 (1986).
4. Y. Hori, K. Kikuchi, and S. Suzuki, *Chem. Lett.*, 1695 (1985).
5. Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, *ibid.*, 897 (1986).
6. R. L. Cook, R. C. MacDuff, and A. F. Sammells, *This Journal*, **135,** 1320 (1988).