

THE ELECTROCHEMICAL REDUCTION OF CO₂ TO CH₄ AND C₂H₄ AT Cu/NAFION ELECTRODES (SOLID POLYMER ELECTROLYTE STRUCTURES)

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The construction of copper/Nafion electrodes (solid polymer electrolyte structures) by an electroless plating method is described. These electrodes were used for the gas phase electrochemical reduction of CO₂ to hydrocarbon products, including CH₄ and C₂H₄. The faradaic efficiencies of the electrodes under ambient conditions with a counter solution of 1 mM H₂SO₄ at a potential of -2.00 V vs. SCE reached a steady-state value of about 20% after 30 min of electrolysis. This corresponded to a rate of total hydrocarbon production of approximately 9.8×10^{-7} mole h⁻¹ cm⁻². Increasing the potential of the electrode to more negative potentials, or increasing the proton concentration of the counter solution, caused a decrease in the faradaic efficiencies due to a relative increase in the rate of proton reduction vs. that of CO₂ reduction. If the proton concentration of the counter solution was decreased to an alkaline pH, hydrocarbon production quickly ceased because of proton starvation.

1. Introduction

We report the construction of copper electrodes, based on solid polymer electrolyte (SPE) technology, that can be used for the gas phase electrochemical reduction of CO₂ to CH₄ and C₂H₄. SPE techniques involve the use of an ion exchange membrane (usually Nafion [1]) with porous contacting electrodes for the construction of electrochemical systems in which ionic migration to maintain charge neutrality occurs within the membrane. The principle is illustrated in fig. 1. The membrane/electrode separates the working chamber, which contains the substrate, and the counter chamber which contains an aqueous electrolyte solution along with the auxiliary and reference electrodes. The membrane is an inert, ion exchange polymer (e.g., Nafion) with metal deposited onto the face that is bathed by a gaseous substrate. When the metal electrode is held at an appropriate potential, the substrate in the working chamber is reduced, coupled with an ionic migration through the membrane to maintain electroneutrality. Concurrently, some species in the counter solution react at the auxiliary electrode. In this way,

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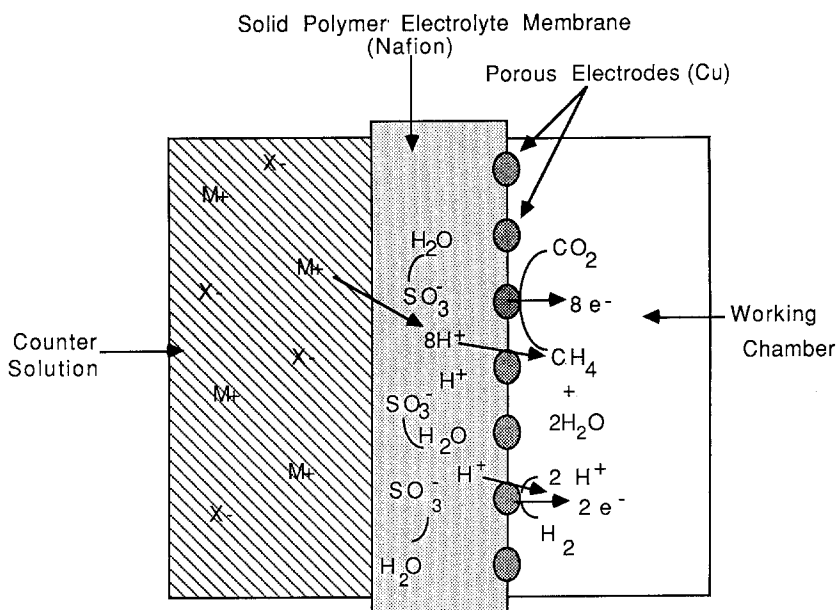
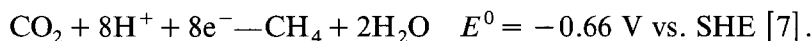


Fig. 1. Schematic diagram of a porous metal electrode supported on a solid polymer electrolyte membrane for the electrochemical reduction of a gas phase substrate.

electrolyses may be carried out in the gas phase, without solvent. The advantages include an increased mass transfer over that in solution, and the absence of solvent or electrolyte impurities which might otherwise poison the catalyst.

Copper-alloy catalysts have shown activity for the hydrogenation of CO, CO₂ and CO/CO₂ mixtures to CH₃OH and CH₄ [2–7]. Copper alone, however, is completely inactive for hydrogenation [2,3]. Its promoting properties are attributed to participation of a partially oxidized copper species [4], or a diluent effect [3]. The standard redox potential of the reduction of CO₂ to CH₄ is given by:



Despite its thermodynamic feasibility, kinetic difficulties arising from multielectron reduction processes are expected to limit the faradaic efficiency. For example, the one-electron reduction of CO₂ to its radical anion occurs at –2 to –3 V vs. SCE.

Because of these considerations, the first report [8] of the direct electrochemical reduction of CO₂ to CH₄ at high purity Cu metal foils from aqueous solutions in high yields led to recent additional studies [9–11]. These studies of the reduction of CO₂ at Cu foil electrodes immersed in KHCO₃ solutions demonstrated that:

1) the major hydrocarbon products are CH₄ and C₂H₄, while the minor products are CO and HCOOH, with no detectable formation of CH₃OH or HCOH [8];

- 2) the potential for onset of CH₄ production is near -1.6 V vs. SCE, while optimal faradaic efficiencies are found at potentials near -2.0 V vs. SCE [9];
- 3) C₂H₄ production increases with increasing temperature, while CH₄ production, and overall hydrocarbon formation efficiencies decrease with increasing temperature [8–10];
- 4) the faradaic yields are controlled by the mass transfer of CO₂ in solution [11].

The experiments reported here, on the gas phase reduction of CO₂ at a Cu/SPE electrode, were motivated by the hope that increased mass transfer in the gas phase and controlled proton flux through the membrane would promote better efficiency and higher stability of the Cu electrode.

2. Experimental

Copper bonded membranes were prepared by an electroless plating method, similar to that used for fabrication of Pt/SPE systems [12]. The solid polymer electrolyte (SPE) membrane material was Nafion 115 (equiv. wt. = 1100, 5 mil thickness; E.I. DuPont de Nemours, Inc., Wilmington, DE), which was cleaned by boiling in concentrated HNO₃ for one hour and then in milli-Q reagent grade water (Continental Water Systems, El Paso, TX) for one hour. The Nafion was clamped between two half cells, with one compartment containing 0.010 M hydrazine (Fisher Scientific, Fair Lawn, NJ) in an aqueous alkaline solution (pH = 13) and the other compartment containing 0.035 M copper (II) (from CuSO₄, anhydrous, Fisher Scientific) in a P₂O₇⁴⁻ (Na₄PO₄ · 10H₂O, MCB Manufacturing Chemists, Cincinnati, OH) plating solution. The copper-pyrophosphate plating solution was similar to that described by Ogden and Tensch [13], but one-tenth the concentration. The cell was allowed to stand for two weeks, with dailing stirring to release bubbles trapped on the membrane surface, and a change of fresh reductant (hydrazine) every 3 to 4 days. During this time copper metal formed on the copper-pyrophosphate solution side. Each Cu/SPE electrode was used for several experiments. After each experiment the copper metal surface was cleaned by rinsing with 1.0 M HCl [9], and stored overnight in a two-compartment cell under the same conditions used for fabrication. Before each experiment, the metal surface was rinsed with 85% H₃PO₄ (Fisher Scientific), 1.0 M HCl, and milli-Q reagent grade water.

An investigation of the surface composition of the Cu/SPE electrode by X-ray photoelectron spectroscopy (XPS) has not yet been carried out. The surface appeared bright and shiny after cleaning, and XPS studies of identically prepared Cu foils showed only signals for Cu metal on the surface. The true area of this porous electrode was estimated by its capacitance, relative to that of a polished Cu dish electrode, in a saturated K₂SO₄ solution by voltammetric scans between

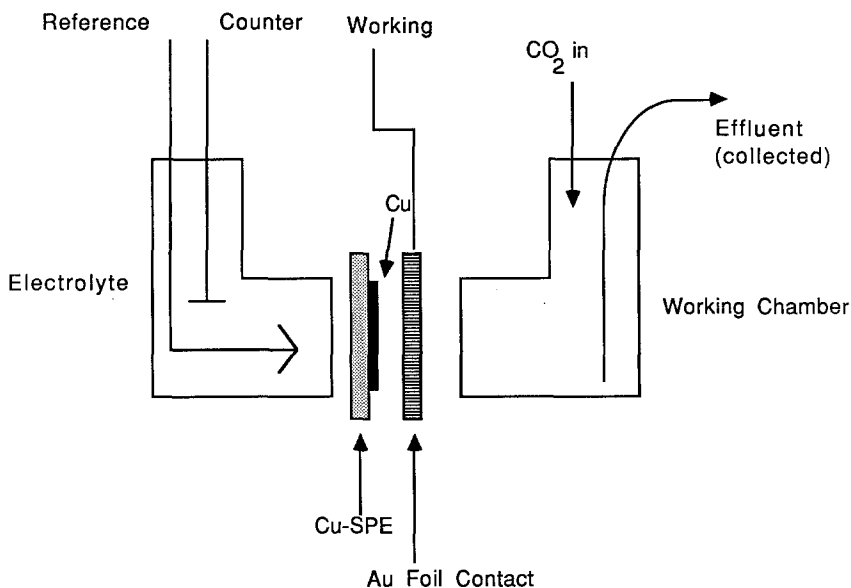


Fig. 2. Electrochemical cell configuration.

-0.10 and -0.20 V vs. SCE. The true area was found to be about 32 cm^2 , corresponding to a roughness factor of 64, similar to previously reported values of Pt/SPE electrodes [14].

The two compartment cell used for all experiments is shown schematically in fig. 2. Between the two half-cells were clamped the copper-solid polymer electrolyte membrane (Cu/SPE) electrode, and a Au ring foil (0.025 mm, 99.99 + %, Alfa Products, Danvers, MA) as an electrical contact. A gas tight gold-to-glass seal was obtained with a thin film of silicone rubber sealant (Silastic 732 RTV, Dow Corning, Midland, MI). The metallized side of the membrane faced the working chamber, which was filled with a continuous flowing stream of gaseous CO_2 . The non-metallized side face the counter chamber, which contained an aqueous electrolyte solution along with the saturated calomel reference electrode (SCE) and a platinum flag counter electrode. Gaseous CO_2 , obtained from the sublimation of dry ice, was humidified by bubbling through 0.5 M KHCO_3 (pH = 9) prior to induction to the working chamber of the electrochemical cell. Effluent gases from this continuous flow system were collected in 25 mL aliquots with inverted test tubes filled with water. Analyses of the hydrocarbon products were performed on a Varian model 1860 gas chromatograph (Varian Associates, Palo Alto, CA) with flame ionization detection. The chromatographic column, a 6 ft. \times 1.8" OD stainless steel column packed with 80/100 mesh Porapak Q (Alltech Associates, Inc., Deerfield, IL), 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 Spectra-Physics SP4270 integrator (San Jose, CA), on the

basis of peak areas, from a linear, 3-point standard curve with triplicate injections. Sample deviation was less than 5%.

All electrolyses were performed under potentiostatic (controlled potential) conditions with an EG&G Princeton Applied Research (PAR, Princeton, NJ) model 173 potentiostat/galvanostat. Electrolytes KHCO₃ (ACS reagent grade, MCB) and H₂SO₄ (ACS reagent grade, Fisher Scientific) were used without further purification. All solutions were made with reagent grade milli-Q water.

3. Results and discussion

Electrolyses were performed under potentiostatic (controlled potential) conditions, while the current and the product concentration in the cell effluent were monitored as a function of time. Faradaic efficiencies were calculated on the basis of 8 electrons consumed per CH₄ formed, 12 equivalents per C₂H₄, and the ideal gas molar volume of 22.4 liters/mole. Figure 3 illustrates the behavior of current and faradaic efficiency vs. time, for a Cu/SPE electrode at room temperature (22°C), held at a potential of -2.00 V vs. SCE, with a counter solution of 1 mM H₂SO₄ (pH = 3). The general shape of the current vs. time profile shown in fig. 3 was observed across the experimental potential range (-1.80 to -2.25 V vs. SCE) for counter solutions of proton concentration 1 to 10 mM (pH = 2 to 3). The time dependence of faradaic efficiency is exaggerated by the 5-10 fold decrease in current during the first 30 min. of electrolysis. Although the efficiency increased by a factor of 15 to 20 to ca. 20%, the actual rate of total hydrocarbon production, measured by its concentration in cell effluent, only approximately doubled over the course of the experiment to a steady-state value of ca. 9.8×10^{-7} mole h⁻¹ cm⁻². The course of the current-time and efficiency-time behavior is probably caused by a decrease in a background process, (e.g., proton reduction of adsorbed acid from the pre-electrolysis cleaning procedure), followed by proton depletion and slow accumulation of reaction intermediates over the course of the multi-electron reduction.

At a more negative potential of -2.25 V vs. SCE, the time dependences of current and faradaic efficiency was similar to that at -2.00 V, but the steady-state current increased by a factor of two, while the faradaic efficiency value was reduced by half. The rate of hydrocarbon production at -2.25 V is about one-quarter that at -2.00 V. Apparently, proton reduction can compete effectively with CO₂ reduction at the more negative potential [8,9].

Decreasing the pH of the counter solution from 3 to 2 did not affect the steady-state current, but the steady-state faradaic efficiencies decreased by 2 to 3-fold. During the electrolysis at pH = 2, some bubbles formed at the back (counter solution) side of the membrane, indicating that proton reduction became the predominant process. When a counter solution of 0.5 M KHCO₃ (pH = 9) was used, hydrocarbon formation ceased after 5 min. of electrolysis. In this

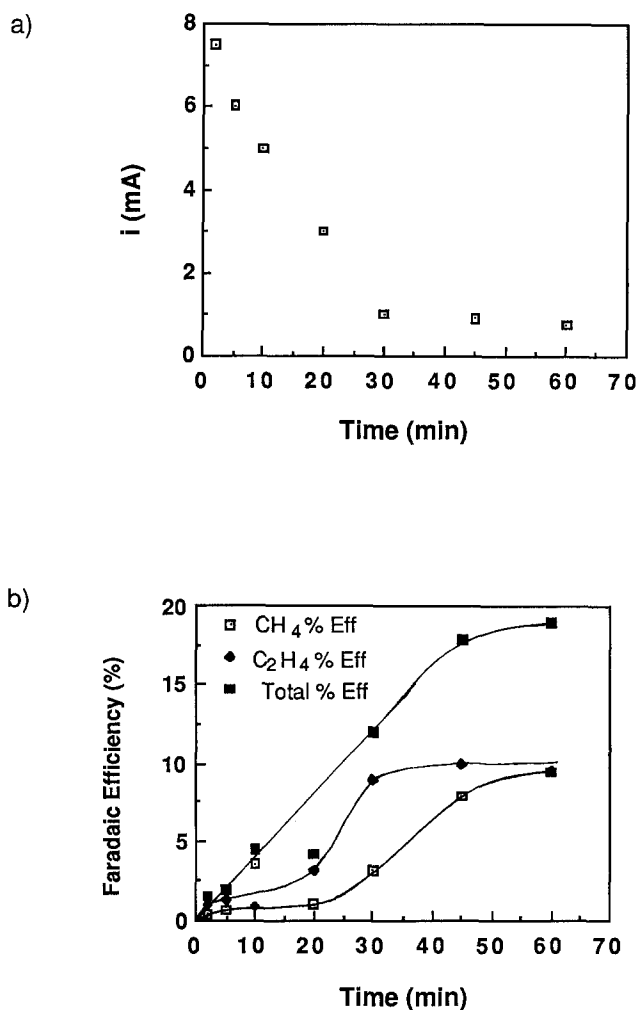


Fig. 3. Dependence of current and faradaic efficiency vs. time at a copper/SPE electrode held at constant potential. Experimental conditions: $E = -200$ V vs. SCE; $T = 22^\circ\text{C}$; CO_2 flow rate = 45 mL/min; counter solution = 1 mM H_2SO_4 ; rest potential of metal electrode before electrolysis = -0.09 V vs. SCE.

counter solution, the concentration of K^+ in solution is much greater than that of protons. Therefore, the majority charge carrier through the SPE becomes K^+ and for every electron transferred to CO_2 at the Cu, one K^+ ion is transferred from the membrane to the electrode surface, instead of a proton. The stoichiometry of CO_2 reduction to CH_4 requires 8 protons for 8 electrons transferred. If the only source of these protons is the water vapor humidifying the gas stream or solvating the Nafion membrane, protons will be depleted quickly, shutting down hydrocarbon production. CO_2 reduction in solution does not suffer from proton depletion, even at high pH's, since rapid water dissociation in the buffered electrolyte provides a large proton reservoir at essentially constant concentration.

The efficiencies we observe for the gas phase reduction of CO₂ are only about onehalf those observed at Cu foil electrodes in solution. The problem appears to be that high acidities in the counter solution promote competitive proton reduction at the Cu, while higher pH's lead to proton starvation at the Cu electrode.

Acknowledgement

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