

## SHORT COMMUNICATION

**The electroreduction of carbon monoxide at metal/zirconium hydrogen phosphate interfaces**

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**1. Introduction**

Catalytic hydrogenation of carbon monoxide is an industrial method for the production of hydrocarbons and alcohols. The process is carried out typically at 100–200 atm and 200–400°C [1]. Electroreduction of carbon monoxide in aqueous solution at ambient temperature and pressure has been reported recently [2–6]. Investigation of the electrochemical route is interesting because it occurs at a lower temperature and pressure than the catalytic process, and it provides an insight into the fundamental relationships between heterogeneous catalysis and electrochemistry. This insight may be extended by an investigation of the electroreduction of carbon monoxide at the metal/solid proton-conducting electrolyte interface. There has been only one report in the literature on this topic [7]. The present study investigates the electroreduction of carbon monoxide at the  $M/Zr(HPO_4)_2 \cdot H_2O$  interface (where  $M = Cu, Zn, Cd, Fe$ , and brass (Cu60/Zn40)).

The standard reduction potentials for the reduction of carbon monoxide are easily calculated from the Gibbs energies of formation of the products from CO (g) and H<sub>2</sub> (g) [8]. For reactants and products in the *gas phase* and at room temperature these are as follows: CO/CH<sub>3</sub>OH –0.385 V (a 4e<sup>–</sup> reaction); CO/CH<sub>4</sub> +0.246 V (6e<sup>–</sup> reaction); CO/C<sub>2</sub>H<sub>4</sub> +0.149 V (8e<sup>–</sup> reaction) and CO/HCHO –0.125 V (2e<sup>–</sup> reaction). These values are close to that of the standard hydrogen electrode. Since the hydrogen evolution reaction competes with the reduction of carbon monoxide, and is usually the dominant process [2, 4], metals which exhibit a high overpotential for the hydrogen evolution reaction may be promising electrode materials, e.g. Cu, Ag, Zn, Cd, and Pb [9].

The electrolyte used must have appreciable protonic conductivity, and be stable to electrochemical oxidation and reduction. These criteria preclude the use of antimony oxide hydrates and heteropolyacids such as dodecatungsto-phosphoric and -silicic acids. Solid polymer electrolytes could be ideal, but experiments with Nafion®† indicate that its conductivity drops during reduction (probably as a result of dehydration).  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (abbreviated to ZrP) was

used as the electrolyte in these experiments. Depending on method of preparation, it has a conductivity 10<sup>–3</sup>–10<sup>–5</sup> S cm<sup>–1</sup> at ambient temperature, and good moisture retaining characteristics [10].

**2. Experimental details**

Following Clearfield and Stynes [11], zirconyl chloride octahydrate (45 g) dissolved in 100 cm<sup>3</sup> of 2 mol dm<sup>–3</sup> hydrochloric acid was slowly added with vigorous stirring to 200 cm<sup>3</sup> of a mixture 2 mol dm<sup>–3</sup> in HCl and 4 mol dm<sup>–3</sup> in orthophosphoric acid. The gelatinous precipitate produced was filtered, and washed six times with 2% H<sub>3</sub>PO<sub>4</sub>. After drying at 110°C for 48 h, the initial (amorphous) precipitate was refluxed in 6 mol dm<sup>–3</sup> H<sub>3</sub>PO<sub>4</sub> for 20 h, to yield microcrystalline ZrP as confirmed by X-ray powder diffraction. The microcrystalline product was washed repeatedly with deionised water and dried at 110°C for 48 h before being used as the electrolyte in the cell.

The electrode for the electroreduction of CO consisted of the metal powder intimately ground with ZrP in the mass ratio 7:3. This electrode configuration provides an enhancement of the three-phase boundary over that for plane sheet or grid electrodes. The metals used were: Cu (99.9%, 10 μm, Aldrich), Zn (99%, 10–25 μm, BDH), Fe (99.9%, 325 mesh, Aldrich), Cd (99.5%, 325 mesh, Aldrich), and brass (99.9%, 75 μm, Goodfellow). The current collector for the working electrode consisted of a 200 mesh Ni grid with Ni tag spot-welded to it. A high purity platinum grid (100 mesh, Johnson Matthey) with a Pt foil tag was used as the (hydrogen) counter electrode. The electrolyte was intimately ground with 20% by weight of PTFE powder (0.5 μm, BDH) to give pellets with a low permeability to gaseous hydrogen. The electrodes and electrolyte were pressed together in a purpose-built die at 500–600 MPa to form a sandwich 1.2–1.5 mm thick (schematically shown in Fig. 1). The sandwich was mounted in an ambient temperature cell (shown in Fig. 2), with gas-tight compartments for CO and H<sub>2</sub>, and with minimum head space above the electrode surfaces to ensure good contact between the flowing gases and the electrode. The grid current collectors gave sufficient reinforcement to the

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† Nafion® is the registered trademark of DuPont for its perfluorocarbonsulphonic acid polymers.

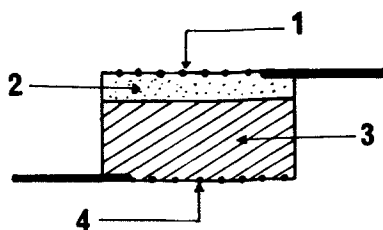


Fig. 1. Schematic structure of the electrode-electrolyte manifold. (1) Ni grid and tag, (2) metal-electrolyte electrode, (3) electrolyte and (4) Pt grid and tag.

sandwich to prevent disintegration or the formation of cracks.

Carbon monoxide (research grade, BOC) and hydrogen (commercially pure, BOC) were used without further purification. The hydrogen was bubbled through distilled water to keep the electrolyte hydrated. Gas flows could be controlled in the range 0–50 ml min<sup>-1</sup> using mass-flow controllers (High-Tech B.V.). The electrolysis was carried out in the galvanostatic mode using a PAR 173 potentiostat/galvanostat. The products of electroreduction of CO were injected through a sample loop into a gas-chromatograph (Philips PU 4400) equipped with a Poropak-Q packed column for the separation of permanent gases and water, and a wall-coated fused silica capillary column for the separation of higher hydrocarbons and alcohols. The pipe through which the products flowed from the cell to the chromatograph was kept at 60–70°C to avoid condensation of the less volatile products.

### 3. Results and discussion

Analyses of products of electroreduction of CO at various metal electrodes are presented in Table 1. In order to evaluate Faradaic efficiencies, the leak of

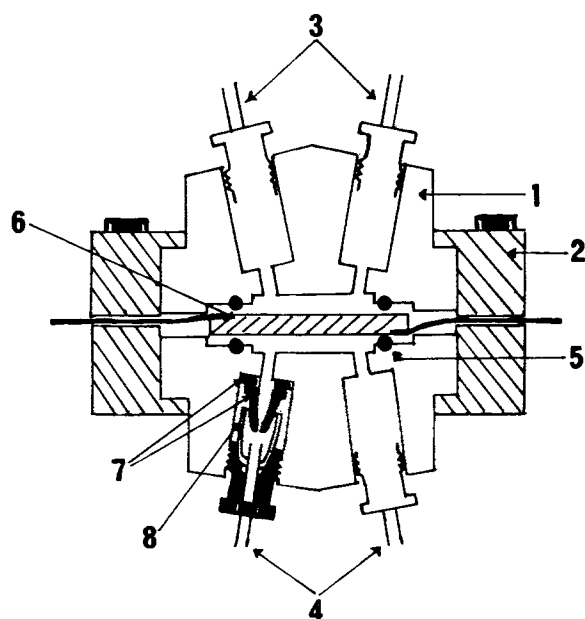


Fig. 2. Cross-section of the electrochemical cell. (1) PTFE body, (2) Kel-F flanges with screws, (3) PTFE tube inlet/outlet for CO, (4) PTFE tube inlet/outlet for H<sub>2</sub>, (5) Viton O-rings, (6) electrode-electrolyte manifold and (7) sealing Kel-F ferrules/washers (identical at all four gas ports).

Table 1. The products of electroreduction of CO at the M/Zr(HPO<sub>4</sub>)<sub>2</sub>-H<sub>2</sub>O interface\*

Current density (mA cm <sup>-1</sup> )	Metal	Faradaic efficiency			
		H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	HCHO	C <sub>8</sub> -C <sub>10</sub>
100	Cu	72.5	2.5	25.0	—
	Zn	98.0	—	—	—
	Cd	92.0	5.0	—	~3 (0.2 butanol)
	Fe	87.0	13.0	—	—
	Brass	86.0	4.6	10.3	traces
75	Cu	86.0	3.0	11.0	—
	Zn	98.6	—	—	traces
	Cd	94.0	3.6	—	~3 (0.5 butanol)
	Fe	95.7	1.4	—	~3
	Brass	100	—	—	traces
50	Cu	78.0	1.6	20.0	—
	Zn	96.0	3.8	—	—
	Cd	98.0	—	—	~2
	Fe	95.0	—	—	~5
	Brass	95.2	3.7	—	—
30	Cu	76.6	3.2	20.0	—
	Cd	96.5	—	—	~3
	Fe	99.0	—	—	~1
	Brass	98.6	—	—	traces
20	Cu	91.0	8.8	—	—
	Fe	97.6	2.0	—	~0.2
	Brass	99.4	—	—	~0.4

\* Over an electrode of geometrical area 1.33 cm<sup>2</sup>.

hydrogen across the pellet was accurately determined for each of the pellets used. The possibility of heterogeneous catalysis of the reaction between CO and H<sub>2</sub> in the cathode compartment and product pipe was examined using a mixed feed without current being passed. Only carbon monoxide, hydrogen and water were detected, *i.e.* no products formed in the absence of electrical current. Table 1 shows that the nature of products detected at any particular current density is dependant on the metal present in the electrode.

Formaldehyde and ethylene were produced at considerable efficiencies on Cu (at almost all current densities) and on brass at 100 mA cm<sup>-2</sup>. The similarity in the behaviour of brass and Cu at high current densities illustrates the importance of the chemical nature of the metal site in determining the nature of the products. This is analogous to the selectivity characteristics of heterogeneous catalysts. In aqueous systems, methanol and methane have been reported at Cu electrodes [4]. In this work neither was detected. At room temperature and pressure, the Gibbs energy change for reaction ( $\Delta G_m^0$ ) of CO (g) and H<sub>2</sub> (g) to give aqueous methanol is -25 kJ mol<sup>-1</sup>, while that to give CH<sub>3</sub>OH (g) is +149 kJ mol<sup>-1</sup> [8]. The corresponding values for formation of formaldehyde are +86 kJ mol<sup>-1</sup> [HCHO (aq)], and +24 kJ mol<sup>-1</sup> [HCHO (g)]. From these calculated figures it follows that the preferred product in aqueous systems is methanol, and in the gas phase it is formaldehyde. These predictions are born out by observation. Ethylene is detected for all the electrodes to varying extents depending on the current density.

This suggests the formation of a  $\text{CH}_2$  intermediate in the process. This is also consistent with the production of HCHO.  $\text{C}_6$ - $\text{C}_{10}$  alcohols were produced on Cd and Fe at considerable efficiencies for all current densities. If  $\text{CH}_2$  is involved in the reactions, the inference is that the intermediate is relatively stable on these metal surfaces.

High faradaic efficiencies for hydrogen evolution are observed for all the electrode metals, but efficiencies do not follow the trend predicted from overpotential data in aqueous protonic electrolytes such as  $\text{H}_2\text{SO}_4$ , HCl, and NaOH [9]. This indicates that the choice of a solid proton-conducting electrolyte influences the kinetics of the electrochemical process.

#### 4. Conclusion

Electroreduction of CO at the Cu/ZrP interface shows significant preference for the production of formaldehyde and ethylene. The corresponding Cd and Fe systems produce higher alcohols. The dependence of the nature and amount of products on the metal electrode and current density indicates a link between heterogeneous catalysis and electrochemistry, and the possibility of using electrochemical studies to investigate and design heterogeneous catalytic systems.

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#### References

- [1] 'Kirk-Othmer Encyclopedia of Chemical Technology', 3rd edition, Vol. 11, John Wiley and Sons, New York (1985) p. 473.
- [2] G. A. Kolyagin, B. G. Danilov and B. L. Kornienko, *Elektrokhimiya* **21** (1985) 133.
- [3] H. Yoneyama, K. Wakamoto, N. Hatanaka and H. Tamura, *Chem. Lett.* **6** (1985) 539.
- [4] Y. Hori, A. Murata, R. Takahashi and S. Suzuki, *J. Amer. Chem. Soc.* **109** (1989) 5062; *Chem. Lett.* **8** (1987) 1665.
- [5] J. J. Kim, D. P. Summers and K. W. Friese, *J. Electrochem. Soc.* **245** (1988) 223.
- [6] H. Noda, S. Ikeda, Y. Oda and K. Ito, *Chem. Lett.* (1989) 289.
- [7] M. B. Demidov, E. N. Savinov and V. N. Parman, *React. Kinet. Catal. Lett.* **38** (1989) 295.
- [8] 'The C.R.C. Handbook of Chemistry and Physics', 63rd edition (edited by R. C. Weast), C.R.C. Press, Boca Raton, FA (1982) p. D60-D73.
- [9] A. N. Frumkin, *Adv. Electrochem. and Electrochem. Eng.* **3** (1963) 1263.
- [10] M. Casciola and D. Bianchi, *Solid State Ionics* **17** (1985) 287.
- [11] A. Clearfield and J. A. Stynes, *Inorg. Chem.* **26** (1964) 117.