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Use of gas-diffusion electrodes for high-rate electrochemical reduction of carbon dioxide. II. Reduction at metal phthalocyanine-impregnated electrodes

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The use of polytetrafluoroethylene-bonded, carbon gas-diffusion electrodes, prepared with carbon impregnated with metal phthalocyanines, for the electrochemical reduction of carbon dioxide in aqueous, acidic solution has been investigated. High rates of reduction of carbon dioxide to carbon monoxide were demonstrated at electrodes impregnated with cobalt(II) phthalocyanine. In contrast, formic acid, and not carbon monoxide, was produced at low rates at electrodes impregnated with either manganese, copper or zinc phthalocyanine. This marked variation in reaction product on changing the central metal ion of the organometallic complex is rationalized in terms of a reaction mechanism involving, as the first step, the electrochemical reduction of cobalt(II) to cobalt(I).

1. Introduction

Formic acid or its salts are the major products formed during the direct electrochemical reduction of carbon dioxide in aqueous environments (for a recent review see [1]). In contrast, oxalate and carbon monoxide are obtained, together with some formate, when carbon dioxide is reduced in aprotic solvents such as dimethylformamide [2, 3], acetonitrile [4], dimethyl sulphoxide [5, 6] and propylene carbonate [7]. Amatore and Savéant [8] have recently discussed a possible mechanism for the latter reaction and concluded that it involves three competing pathways: (i) oxalate formation through self-coupling of carbon dioxide anion radicals, (ii) carbon monoxide formation via oxygen–carbon coupling of the anion radical with unreacted carbon dioxide, and (iii) formate formation through protonation of the anion radical by residual water.

Several workers have investigated the electrochemical reduction of carbon dioxide in aqueous electrolytes in the presence of a variety of organometallic complexes. Takahashi *et al.* [9] reported that carbon dioxide is reduced to formate at mercury cathodes in the presence of cobalt mesotetracarboxyphenylporphyrin. Fisher and Eisenberg [10] found that a variety of cobalt- and nickel-tetra-azamacrocyclic complexes catalysed the reduction of carbon dioxide to carbon monoxide. Conflicting results have been reported using carbon electrodes impregnated with metal phthalocyanines. Meshitsuka and co-workers [11] were able to produce oxalate and glycolate at carbon electrodes impregnated with either cobalt(II) or nickel phthalocyanine. Lieber and Lewis [12] reported that the major reduction product at carbon electrodes impregnated with cobalt(II) phthalocyanine was carbon monoxide, with only trace amounts of oxalate and formate being formed. In contrast, Kapusta and Hackerman [13] could only detect formate and methanol amongst the reaction products, using almost identical reaction conditions. None of these authors proposed a reaction mechanism to account for their differing product distribution.

In Part I [14] we demonstrated that carbon dioxide may be reduced to formic acid at high current efficiency and at high current densities at polytetrafluoroethylene (PTFE)-bonded, carbon gas-diffusion electrodes impregnated with either lead, indium or tin. In this paper we present the results of our investigation into the electrochemical reduction of carbon dioxide at PTFE-bonded, gas-diffusion electrodes prepared from carbon impregnated with either cobalt(II), copper, zinc or manganese phthalocyanine.

2. Experimental details

2.1. *Electrode preparation*

The metal phthalocyanines used in this investigation were commercially available compounds (Eastman Kodak) and were used as received.

The gas-diffusion electrodes were prepared in the following manner. Carbon black (Vulcan XC 72, Cabot Carbon, 6 g) was added to a stirred solution of the appropriate metal phthalocyanine (0.3 g) dissolved in 98% sulphuric acid (~ 20 ml). The resulting mixture was poured quickly into water (~ 500 ml) to precipitate the metal phthalocyanine onto the carbon substrate. The impregnated carbon was subsequently filtered, washed and dried. A 5 g sample of the impregnated carbon was micronized for 10 min in 45 g of water to form a uniform slurry. Then 1.4 g of a PTFE dispersion (Fluon, GP 1, ICI) was added, with gentle stirring, to 10 g of the slurry to give a thick paste. A small quantity of this paste was spread onto a lead-plated nickel gauze (area ~ 3.2 cm^2), dried and compacted onto the gauze until the carbon layer was firmly embedded onto the current collector. This procedure was repeated until the required loading had been achieved. The electrodes were then cured in a tube furnace in a nitrogen atmosphere at 300° C for 3 h before being given a final compression at a pressure of approximately 10^5 kPa.

2.2. *Experimental procedure*

The electrolysis cell, electrochemical instrumentation and mode of operation have been described elsewhere [14]. All electrode potentials are quoted with respect to the saturated calomel electrode (SCE).

The electrochemical reduction of carbon dioxide was performed at room temperature (~ 20° C) in dilute sulphuric acid (pH 2) containing 50 $\mathrm{g\,l^{-1}}$ sodium sulphate.

To estimate the amounts of gaseous products formed on the gas side of the electrodes, the carbon dioxide exit stream was sampled and its carbon monoxide and hydrogen content was determined by gas chromatography. The catholyte solutions were analysed quantitatively for their formic acid content by high pressure liquid chromatography (HPLC) as described elsewhere [14] and for their oxalic acid content by derivatizing aliquots of the catholyte with *o*-phenylene diamine and analyzing the resulting solution by HPLC [15].

3. Results

3.1. *Cobalt(II) phthalocyanine-impregnated electrodes*

Carbon monoxide and hydrogen were the only significant products formed when carbon dioxide was reduced at a PTFE-bonded, carbon gas-diffusion electrode impregnated with cobalt(II) phthalocyanine. The electrode was potentiostated successively at -1.50, -1.70, -1.90, -2.10 and -2.20 V and the carbon dioxide exit stream sampled and subsequently analysed. The results presented in Table 1 show that the relative amounts of carbon monoxide and hydrogen depended on the cathode potential, with considerably more hydrogen produced as the cathode potential was increased from -1.50 V (partial hydrogen current density = 3 $\mathrm{mA\,cm^{-2}}$ at a current efficiency of 14%) to -2.20 V (partial hydrogen current density = 99 $\mathrm{mA\,cm^{-2}}$ at a current efficiency of 72%). However, the partial current density for the production of carbon monoxide was almost independent of the electrode potential, varying randomly between 19 and 26 $\mathrm{mA\,cm^{-2}}$. (Inaccuracies inherent in the method used to calculate the partial current densities and hence current efficiencies account for the variations at each potential.)

Insignificant quantities of gas were evolved from the wet side of the electrode during the

Table 1. Effect of electrode potential on the reaction products (H_2 and CO) at a PTFE-bonded, gas-diffusion electrode impregnated with cobalt(II) phthalocyanine

Electrode potential[a] *(V versus SCE)*	*Measured current density ($mA\ cm^{-2}$)*	*Current efficiency (%)*		*Partial current density ($mA\ cm^{-2}$)*	
		H_2	*CO*	*H_2*	*CO*
−1.50	22	14	100	3	22
−1.70	33	20	79	7	26
−1.90	53	45	48	24	25
−2.10	94	71	24	67	23
−2.20	137	72	14	99	19

[a] Controlled potential electrolysis in $50\ g\ l^{-1}$ Na_2SO_4 acidified to pH 2 with H_2SO_4.

electrolyses. Analysis of the catholyte at the end of the experiment indicated that no formic acid or oxalic acid had been produced.

These observations were confirmed by repeating the electrolysis experiments using three different electrode samples. The results presented in Table 2 show that the amounts of carbon monoxide and hydrogen produced varied from sample to sample, reflecting the probable variations in the exact composition of the different electrodes. Again, neither formic acid nor oxalic acid were produced at any of the cobalt(II) phthalocyanine-impregnated electrodes.

3.2. *Manganese, copper and zinc phthalocyanine-impregnated electrodes*

In contrast, both formic acid and hydrogen, but no carbon monoxide, were produced at a PTFE-bonded, carbon gas-diffusion electrode impregnated with manganese phthalocyanine maintained at −2.00 V. The current efficiency for formic acid production was estimated to be 26% with a partial current density of $4\ mA\ cm^{-2}$. Analysis of the carbon dioxide exit stream revealed that the major reduction product was hydrogen. The partial current density for hydrogen production was estimated to be $12\ mA\ cm^{-2}$, corresponding to a current efficiency of 77%.

A preliminary series of experiments was performed using some electrodes impregnated with either copper or zinc phthalocyanine. Unfortunately, the carbon dioxide exit streams were not analysed for either their carbon monoxide or hydrogen content, but analysis of the catholytes showed that some formic acid had been produced. At the copper phthalocyanine-impregnated electrodes, the current efficiency for formic acid production varied between 13 and 38% with partial current densities of $3-22\ mA\ cm^{-2}$. At the zinc phthalocyanine-impregnated electrodes, the current efficiency was only 5% with a partial current density of $1\ mA\ cm^{-2}$.

Hydrogen evolution from the wet side of the electrode was evident at the majority of the manganese, copper and zinc phthalocyanine-impregnated electrodes.

Table 2. Reduction of carbon dioxide at PTFE-bonded, carbon gas-diffusion electrodes impregnated with cobalt(II) phthalocyanine

Electrode	*Electrode potential*[a] *(V versus SCE)*	*Current efficiency (%)*				*Partial current density ($mA\ cm^{-2}$)*	
		Formic acid	*Oxalic acid*	*H_2*	*CO*	*H_2*	*CO*
1	−1.80	0	0	8	67	4	36
2	−1.80	0	0	55	24	38	16
3	−2.00	0	0	21	74	16	55

[a] Controlled potential electrolysis in $50\ g\ l^{-1}$ Na_2SO_4 acidified to pH 2 with H_2SO_4.

4. Discussion

Carbon dioxide is reduced to carbon monoxide at PTFE-bonded, carbon gas-diffusion electrodes impregnated with cobalt(II) phthalocyanine; no significant amounts of either formic acid or oxalic acid were produced. In contrast, varying amounts of formic acid were produced at similar electrodes prepared using carbon impregnated with either manganese, copper or zinc phthalocyanine. These results may be compared with those obtained for the reduction of carbon dioxide at PTFE-bonded, carbon gas-diffusion electrodes impregnated with either lead, tin or indium. As we have reported in Part I [14], carbon dioxide is reduced to formic acid in high yield and at high rates at these electrodes.

These observations indicate that the reaction mechanism for the reduction of carbon dioxide at electrodes impregnated with cobalt(II) phthalocyanine is significantly different to that occurring at electrodes impregnated with manganese, copper or zinc phthalocyanine as well as with metallic lead, indium or tin. The variation in product distribution on changing the central metal ion of the phthalocyanine complex is not entirely unexpected, since it is known that their electrochemical behaviour depends upon the metal ion [16–18]. The cathode potentials used in this investigation (-1.50 to -2.20 V) are considerably more negative than the first reduction potentials for these complexes. The work of Rollmann and Iwamoto [16] has shown that, in the case of cobalt(II) phthalocyanine, the metal ion is the electroactive centre and is reduced to cobalt(I), whereas for all the other complexes the phthalocyanine ring is reduced to its radical anion.

Lieber and Lewis [12] reported that the cyclic voltammetric behaviour of cobalt(II) phthalocyanine in the presence of carbon dioxide was identical to that recorded in the absence of carbon dioxide, thereby precluding the possibility of any strong interaction between cobalt(I) phthalocyanine and carbon dioxide. Similar conclusions may be drawn from the results of the *in situ* Raman spectroscopic studies of the reduction of carbon dioxide at cobalt(II) phthalocyanine-impregnated, gas-diffusion electrodes [19]. The Raman spectrum recorded from an electrode polarized at a potential of -1.80 V was identical to that recorded from chemically produced cobalt(I) phthalocyanine. Exposing the gas side of the electrode to an atmosphere of carbon dioxide did not cause any further alterations to the Raman spectrum.

Chemically produced cobalt(I) phthalocyanine has been used to reduce a variety of functional groups [20], but not, as far as we are aware, to reduce carbon dioxide. Cobalt(I) phthalocyanine is a strong nucleophile [21], hence it would be expected to react readily with carbon dioxide, leading to the formation of a cobalt(III)–CO_2^-–phthalocyanine complex. Protonation, followed by a second electron and proton transfer reaction, would yield carbon monoxide and water and regenerate the cobalt(II) phthalocyanine catalyst.

The maximum rate of reduction of carbon dioxide which can be achieved at solid electrodes immersed in aqueous solutions is severely restricted by the low solubility of carbon dioxide in water. Utilization of the concept of the gas-diffusion electrode has enabled us to develop electrodes capable of reducing carbon dioxide to formic acid at current densities in excess of $100\,\mathrm{mA\,cm^{-2}}$ [14]. Inspection of the partial current densities for the reduction of carbon dioxide to carbon monoxide presented in Tables 1 and 2 reveals that a similar, but not quite so large, increase in current density has been achieved at the PTFE-bonded electrodes impregnated with cobalt(II) phthalocyanine. The results presented in Table 1 show that the partial current density is independent of potential in the range -1.50 to -2.20 V. This indicates that the current is limited by the rate of transport of carbon dioxide through the electrode. It is also apparent that a second electrolytic reaction, i.e. the reduction of water to hydrogen, became progressively more important as the potential of the electrode was made more negative.

Only small amounts of formic acid were produced at the gas-diffusion electrodes impregnated with the other metal phthalocyanines used in this investigation. The partial current densities for the formation of formic acid of these electrodes are very similar to those reported for the formation of formic acid at unimpregnated PTFE-bonded electrodes [14], indicating that the metal phthalocyanine plays little or no role in catalysing the electrochemical reduction of carbon dioxide.

5. Conclusion

Carbon dioxide can be reduced selectively in aqueous electrolytes to carbon monoxide at PTFE-bonded, carbon gas-diffusion electrodes impregnated with cobalt(II) phthalocyanine. The reaction mechanism probably involves the formation of a cobalt(I) phthalocyanine intermediate. Formic acid, and not carbon monoxide, was produced at similar electrodes impregnated with manganese phthalocyanine.

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