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Use of gas-diffusion electrodes for high-rate electrochemical reduction of carbon dioxide. I. Reduction at lead, indium- and tin-impregnated electrodes

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The use of metal-impregnated polytetrafluoroethylene-bonded carbon gas-diffusion electrodes for the electrochemical reduction of carbon dioxide in aqueous solution has been investigated over a wide range of pH (1 to 5). High rates of reduction of carbon dioxide to formic acid were demonstrated. Lead-impregnated electrodes operated at 115 mA cm^{-2} in an aqueous acidic electrolyte (pH 2) selectively produced formic acid with a current efficiency of nearly 100% at an *iR*-corrected potential of approximately − 1.8 V versus saturated calomel electrode. Electrodes impregnated with either indium or tin produced formic acid at rates comparable with those containing lead. However, in addition to formic acid, small quantities of carbon monoxide were also produced and the simultaneous production of hydrogen by the reduction of water was more significant. Thus, it appears that the electrocatalytic activity for the electrochemical reduction of carbon dioxide to formic acid is lead > indium ~ tin.

1. Introduction

The electrochemical reduction of carbon dioxide has been the subject of investigation by several authors [1–12]. Formate ion is the principal product in neutral aqueous electrolytes, with the highest current efficiencies being obtained at those electrode materials which exhibit high hydrogen overvoltages, e.g. mercury and lead. The low solubility of carbon dioxide in the reaction medium, coupled with the rapid onset of hydrogen evolution as the acidity of the electrolyte is increased, has not only limited the maximum current density to about 1 mA cm^{-2} but has also restricted previous investigators to using catholytes with pH values of not less than about 4 [4, 7]. The mass transport limitation has been partially alleviated by either rotating the cathode [5] or by increasing the partial pressure of the carbon dioxide [9]. However, neither method provides a satisfactory way of increasing the rate of mass transport of carbon dioxide to the electrode surface.

Polytetrafluoroethylene (PTFE)-bonded gas-diffusion electrodes were developed for overcoming similar mass transport limitations in hydrogen–oxygen fuel cells [13]. These electrodes are both porous and hydrophobic and have a structure which not only allows extensive utilization of the electrocatalyst but also increases the area of the three-phase interface between the gas, electrode and electrolyte [14], the region in the electrode where the reaction proceeds. Hence they are capable of operating at high current densities at atmospheric pressure. Despite their well-known use in fuel cells, they have not been extensively employed in other applications where the maximum current density is severely limited by the low solubility of the reactant gas in the electrolyte.

As far as we are aware, no attempt has been made to develop electrodes capable of reducing carbon dioxide in relatively acidic solutions, i.e. those with a pH value of less than about 2. Reduction of carbon dioxide in acidic solution

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would allow the direct production of formic acid without the need for any subsequent acidification step; the protons required to complete the reaction are produced at the oxygen-evolving anode:

$$CO_2 + 2H^+ + 2e \longrightarrow HCO_2H \qquad (1)$$

$$H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e \qquad (2)$$

Lead, indium and tin exhibit high overvoltages for the hydrogen evolution reaction [15]. Previous workers have reported that these metals catalyse the electrochemical reduction of carbon dioxide to the formate ion in neutral solution [3, 11]. In this paper we discuss the electrochemical reduction of carbon dioxide to formic acid at lead-, indium- and tin-impregnated, PTFE-bonded, carbon gas-diffusion electrodes in aqueous, acidic media.

2. Experimental details

2.1. *Electrode preparation*

In this work, the percentage of metal electrocatalyst is calculated from its amount in the metal–carbon mixture. The percentage of PTFE is calculated from the amount of PTFE in the metal–carbon–PTFE mixture.

2.1.1. Carbon electrodes. A series of PTFE-bonded, carbon gas-diffusion electrodes containing either 15, 20 or 30 wt % PTFE was prepared in the following manner. To a suspension of carbon black (5 g, Vulcan XC 72, Cabot Carbon) in 45 g water was added, with gentle stirring, the calculated quantity of a PTFE dispersion (Fluon, GP1, ICI) to give a thick paste. The paste was repeatedly applied onto a lead-plated, nickel gauze current collector (area ~3.2 cm^2), carefully drying the electrode in a stream of warm air after each application. When the required amount of material had been applied, the electrodes were cured in a tube furnace in a nitrogen atmosphere at a predetermined temperature (200, 250 or 300° C) for 1 h before being finally compressed at a pressure of approximately 10^5 kPa.

2.1.2. Lead-impregnated electrodes. The lead-impregnated, PTFE-bonded, carbon gas-diffusion electrodes evaluated in this investigation were prepared by the following methods.

(I) A series of electrodes containing either 10, 30 or 50 wt % lead and 30 wt % PTFE was prepared by adding, with gentle stirring, carbon black (5 g, Vulcan XC 72) and the predetermined amount of PTFE dispersion to the calculated amount of lead nitrate dissolved in ~5 ml water. A small quantity of the resulting paste was transferred to a lead-plated, nickel gauze current collector and dried in a stream of warm air. The dried material was pressed onto the metal gauze. This procedure was repeated several times until the required loading had been achieved. The electrodes were then cured in a tube furnace in a hydrogen atmosphere at 300° C for 3 h before being finally compressed at a pressure of approximately 10^5 kPa.

(II) A series of electrodes containing 50 wt % lead and either 20, 25, 30, 35 or 40 wt % PTFE was prepared in the following manner. A highly dispersed carbon slurry was prepared by micronizing a suspension of carbon black (5 g, Vulcan XC 72) in 45 g water for 10 min. To 20 g of this suspension was added, with gentle stirring, 3.2 g lead nitrate (dissolved in ~5 ml water) and the predetermined amount of the PTFE dispersion to give a thick paste. A small quantity of the paste was applied to a lead-plated, nickel gauze current collector and, after drying, was compacted 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 cured in a tube furnace in a hydrogen atmosphere at 300° C for 3 h before being given a final compression at a pressure of ~3×10^5 kPa.

2.1.3. Indium-impregnated electrodes. A series of indium-impregnated, PTFE-bonded carbon electrodes containing ~50 wt % indium and 30 wt % PTFE was prepared in a manner similar to that described in method II, using a paste containing indium trichloride (2.93 g), PTFE dispersion (2 g) and XC 72 carbon slurry (20 g). The electrodes were cured in a tube furnace in a hydrogen atmosphere at either 140, 250 or 300° C for 3 h. The cured electrodes were given a final compression at ~10^5 kPa.

2.1.4. Tin-impregnated electrodes. Tin-impregnated electrodes, containing 50 wt % tin and 30 wt % PTFE were prepared in a similar manner from a paste containing tin(II) chloride (1.9 g), PTFE suspension (2.1 g) and XC 72 carbon slurry (20 g). The electrodes were cured in a hydrogen atmosphere at 300° C for 3 h and were compressed at $\sim 10^5$ kPa before use.

2.2. *Experimental procedure*

A number of cell designs were evaluated, the most successful of which had the PTFE-bonded electrode mounted horizontally, wet side facing upwards, thereby allowing any cathodically generated hydrogen to escape from the electrode surface (Fig. 1). To minimize intermixing of the anolyte and catholyte, the anode and cathode compartments were separated by a fine plastic mesh. A carbon rod served as the anode and the reference electrode was a saturated calomel electrode (SCE). Carbon dioxide (Distillers Company, Industrial Grade, > 99.8% pure) was supplied to the gas side of the cathode at 50–100 $cm^3 min^{-1}$ and was vented from the same side at an overpressure of 100–200 Pa.

The reactions were performed at room temperature ($\sim$20° C) in 50 $g l^{-1}$ sodium sulphate solution and dilute sulphuric acid (pH 5.0, 3.0, 2.0, 1.5 or 1.0) containing 50 $g l^{-1}$ sodium sulphate. All solutions were prepared from Analar grade chemicals and distilled water.

The electrochemical measurements were performed with either a Wenking Potentiostat Model ST 72 or a Hi-Tek Instruments Potentiostat Model DT 2101. Unless otherwise stated cathode potentials quoted in this paper are not *iR* corrected. The *iR* corrections were determined by the interrupter technique using a Wenking Double Pulse Generator Model DPC 72 and Gould Digital Storage Oscilloscope Model OS 4100. The electrolysis experiments were performed in either the controlled potential or the controlled current mode; the total quantity of charge passed was measured by using either a home-made integrator or by a Hi-Tek

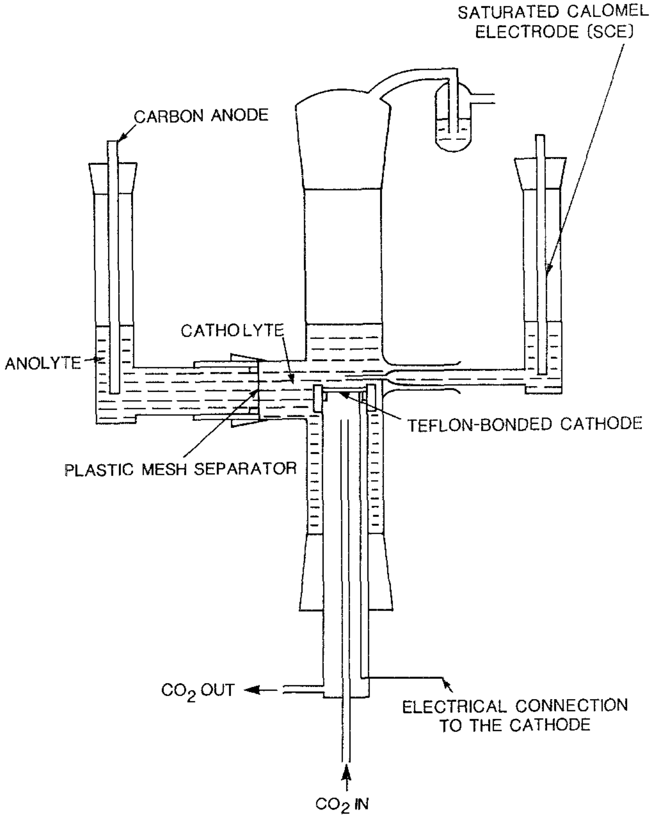

Fig. 1. Electrochemical cell.

Instruments Gated Digital Integrator. The electrolyses were usually terminated after the passage of either 250 or 500 C.

The catholytes were analysed quantitatively for formic acid by high-performance liquid chromatography (HPLC) using an Aminex Ion Exclusion column type HPX-87X (mobile phase 0.0025 M sulphuric acid) coupled to an Applied Chromatography Systems HPLC Monitor fitted with a 254 nm filter. In a number of experiments the carbon dioxide exit gas was sampled and its carbon monoxide and hydrogen content determined by gas chromatography. No attempt was made to measure the amount of hydrogen which evolved from the wet side of the electrodes.

3. Results

The activity of a large number of uncatalysed and lead-, indium- and tin-impregnated electrodes was measured in order to investigate the effect of the metal electrocatalyst on the rate of reduction of carbon dioxide.

3.1. *Uncatalysed gas-diffusion electrodes*

Table 1 summarizes the performance data of some non-impregnated, PTFE-bonded, carbon gas-diffusion electrodes during constant potential electrolysis at -1.80 V. The currents were usually a little greater at the start of the electrolysis experiments and hence, for ease of comparison, average values have been calculated from the total amount of charge passed. Small amounts of formate were detected in the catholytes following controlled potential electrolyses in 50 g l^{-1} sodium sulphate solution. The current efficiency for formate production varied randomly between 0 and 35%, with a maximum partial current density for formate production of 7 mA cm^{-2} being recorded at an electrode containing 15 wt % PTFE cured at 200° C (electrode 1). Carbon monoxide was not produced in any detectable amounts during the electrochemical reduction of carbon dioxide at these non-impregnated electrodes.

Hydrogen evolution was the major reaction occurring at these non-impregnated electrodes. Hydrogen evolution was usually visible on the wet side of the electrodes; no attempt was made to measure the amount of hydrogen produced.

In many cases the gas side of the electrode was damp following the electrolysis experiments, indicating that water had penetrated the electrode structure.

3.2. *Lead-impregnated gas-diffusion electrodes*

High yields of formate were produced at lead-containing electrodes when they were polarized

Table 1. Reduction of carbon dioxide at PTFE-bonded, carbon gas-diffusion electrodes by controlled potential electrolysis at -1.80 V

Electrode	*PTFE (wt %)*	*Curing temperature (° C)*	*Current efficiency formate (%)*	*Partial current density formate (mA cm^{-2})*
1	15	200	31	7
2	15	300	0	0
3	20	200	13	2
4	20	200	22	3
5	20	250	7	3
6	20	250	10	2
7	20	300	0	0
8	20	300	7	1
9	30	200	35	6
10	30	200	0	0
11	30	300	4	0.5
12	30	300	5	0.6
13	30	300	7	1

Electrolyte: 50 g l^{-1} Na_2SO_4.

Table 2. Reduction of carbon dioxide at lead-impregnated, PTFE-bonded, carbon gas-diffusion electrodes by controlled potential electrolysis at − 1.80 V. (Electrodes prepared by method I)

Electrode	*Lead (wt %)*	*Approximate loading ($mg\,cm^{-2}$)*	*Current efficiency formate (%)*	*Partial current density formate ($mA\,cm^{-2}$)*
14	0	50	0	0
15	10	50	41	16
16	30	50	55	14
17	50	50	53	14
18	50	100	89	50
19	50	100	85	36

at − 1.80 V in $50\,g\,l^{-1}$ sodium sulphate solution (electrodes 15 to 19, Table 2). Current efficiencies as high as 55% with a partial current density for formate production of $14\,mA\,cm^{-2}$ were recorded at those electrodes containing either 30 or 50 wt % lead (electrodes 16 and 17). Doubling the electrode loading to approximately 100 mg cm^{-2} resulted in a significant increase in the electrode performance. A current efficiency of 89% at a partial current density of $50\,mA\,cm^{-2}$ was recorded (electrode 18).

3.3. *High-performance, lead-impregnated gas-diffusion electrodes*

The development of gas-diffusion electrodes for fuel cells has shown the advantages of using high surface area catalysts and catalyst supports [13]. Micronizing carbon in water produces a slurry containing carbon particles with a high surface area per unit weight. An electrode preparation technique was developed in which, as the first step, a 10 wt % mixture of carbon in water was micronized. A series of electrodes was prepared using method II (see Experimental section). The effect of changing the catholyte pH (electrodes 20 to 26, Table 3), cathode potential (electrodes 27 to 30, Table 4) and current density (electrodes 31 to 33, Table 5) on the product yield was investigated.

3.3.1. Effect of pH. Current efficiencies for formic acid production in excess of 80% were recorded at those lead-impregnated electrodes (electrode loading $\sim 50\,mg\,cm^{-2}$) polarized at − 1.80 V in $50\,g\,l^{-1}$ sodium sulphate solution acidified to either pH 5.0, 3.0 or 2.0 (electrodes 20 to 22). The partial current density for formic acid production was determined to be approximately 25–30 $mA\,cm^{-2}$.

The electrodes evaluated in more acidic catholytes (pH 1.5 and 1.0) were tested using controlled current, rather than controlled potential, electrolysis conditions. Lower current efficiencies for formic acid production were recorded at $50\,mA\,cm^{-2}$ in the pH 1.5 catholyte (electrodes 23, 54%, and 24, 62%). The (uncorrected) cathode potentials were found to be approximately − 1.85 V. At $100\,mA\,cm^{-2}$ the current efficiency for formic acid production decreased further to 41% (electrode 25). The increase in the rate of reduction of carbon dioxide to formic acid, from $\sim 28\,mA\,cm^{-2}$ (at $50\,mA\,cm^{-2}$) to $41\,mA\,cm^{-2}$ (at $100\,mA\,cm^{-2}$) was more than offset by the rapid increase in the amount of hydrogen evolution. Hydrogen evolution was the predominant reaction (95% current efficiency; formic acid 5%) at $100\,mA\,cm^{-2}$ and pH 1.0 (electrode 26).

All the subsequent electrode evaluation experiments were performed in catholytes whose acidity had been adjusted to pH 2.0.

3.3.2. Effect of electrode potential. The effect of cathode potential on the performance of lead-impregnated electrodes was also evaluated (electrodes 27 to 30, Table 4). Current efficiencies of over 90% were recorded. At one electrode, formic acid was produced at almost 100% current efficiency at a partial current density of $45\,mA\,cm^{-2}$ (electrode 30).

Exceptionally high current efficiencies were also recorded at controlled current experiments at 50 or $115\,mA\,cm^{-2}$ (Table 5). Current efficiency

Table 3. Effect of catholyte pH on the reduction of carbon dioxide at lead-impregnated, PTFE-bonded carbon gas-diffusion electrodes (prepared by method II)

Electrode	*pH*	*Controlled potential electrolysis*			*Controlled current electrolysis*			
		Potential (V versus SCE)	*Current efficiency formate (%)*	*Partial current density formate ($mA\ cm^{-2}$)*	*Applied current density ($mA\ cm^{-2}$)*	*Potential (V versus SCE)*	*Current efficiency formate (%)*	*Partial current density formate ($mA\ cm^{-2}$)*
20	5.0	−1.80	84	27	–	–	–	–
21	3.0	−1.80	81	31	–	–	–	–
22	2.0	−1.80	87	26	–	–	–	–
23	1.5	–	–	–	50	−1.84	54	25
24	1.5	–	–	–	50	−1.86	62	31
25	1.5	–	–	–	100	−2.2	41	41
26	1.0	–	–	–	100	–	5	5

Table 4. Effect of cathode potential on the reduction of carbon dioxide at lead-impregnated PTFE-bonded carbon gas-diffusion electrodes (prepared by method II)

Electrode	*Lead (wt %)*	*Approximate loading (mg cm^{-2})*	*pH*	*Cathode potential (V versus SCE)*	*Current efficiency formic acid (%)*	*Partial current density formic acid (mA cm^{-2})*
27	50	50	2.0	−2.00	91	36
28	50	100	2.0	−2.00	85	57
29	50	100	2.0	−2.10	94	43
30	50	50	2.0	−2.20	100	45

efficiencies of nearly 100% were recorded at two of the electrodes polarized at 115 mA cm^{-2} (electrodes 32 and 33). At 50 mA cm^{-2} (electrode 31) the (uncorrected) cathode potential remained approximately constant at about −2.3 V. However, at 115 mA cm^{-2} (electrode 32) the potential of the cathode rose from −2.7 to −3.0 V during the initial stages of the experiment. The equivalent iR-free cathode potentials are −1.5, rising to −1.8 V. Similar measurements at electrode 33 gave an iR-free cathode potential of −1.2 V at the start of the experiment, quickly rising to a steady state value of about −2.6 V.

3.4. *Indium-impregnated electrodes*

The initial batch of indium-impregnated electrodes was cured in a hydrogen atmosphere at 140° C, i.e. at a temperature below the melting point of indium metal (157° C). However, these electrodes evolved copious quantities of hydrogen on the wet side and subsequently disintegrated when polarized at a potential of −1.80 V in 50 g l^{-1} sodium sulphate (electrodes 34 and 35, Table 6). Two of the electrodes cured at 250° C exhibited similar behaviour (electrodes 36 and 37) whereas a third (electrode 38) produced a small quantity of formate (current efficiency 34% with a partial current density of 11 mA cm^{-2}).

Electrodes cured at 300° C showed a substantially improved performance, with formate and formic acid produced in high yield at reasonably high current densities in both neutral and acidified (pH 2) sodium sulphate catholytes, respectively, (electrodes 39 to 45, Table 6). A current efficiency for formic acid production of 77% with a partial current density of 46 mA cm^{-2} was recorded at an electrode polarized at −1.80 V in 50 g l^{-1} sodium sulphate acidified to pH 2 (electrode 44).

The carbon dioxide exit gas streams from two of the electrolyses were analysed for their hydrogen and carbon monoxide content. Current efficiencies for hydrogen and carbon monoxide production were respectively 22 and 9%, (electrode 43) and 9 and 2%, (electrode 44). Hydrogen evolution from the wet side of the electrode was evident only at electrode 45 which, at −2.00 V, produced formic acid at a current efficiency of 63% with a partial current density of 38 mA cm^{-2}.

Indium-impregnated electrodes were evaluated

Table 5. Effect of current density on the reduction of carbon dioxide at lead-impregnated, PTFE-bonded, carbon gas-diffusion electrodes (prepared by method II)

Electrode	*Lead (wt %)*	*Approximate loading (mg cm^{-2})*	*pH*	*Applied current density (mA cm^{-2})*	*Measured cathode potential (V versus SCE)*	iR-*free cathode potential (V versus SCE)*	*Current efficiency formic acid (%)*
31	50	50	2.0	50	−2.3	NM	94
32	50	50	2.0	115	−2.7 to −3.0	1.5 to −1.8	97
33	50	50	2.0	115	−2.8 to −4.2	−1.2 to −2.6	100

NM: Not measured.

Table 6. Controlled potential reduction of carbon dioxide at indium-impregnated, PTFE-bonded gas-diffusion electrodes

Electrode	*Curing temperature (°C)*	*Electrolyte* ($g\,l^{-1}$ Na_2SO_4)	*pH*	*Potential (V versus SCE)*	*Current efficiency formate (%)*	*Partial current density formate* ($mA\,cm^{-2}$)	*Current efficiency of exit gas (%)*	
							H_2	*CO*
34	140	50	7.0	−1.80	0	0	NM	NM
35	140	50	2.0	−1.80	0	0	NM	NM
36	250	50	2.0	−1.80	0	0	NM	NM
37	250	50	2.0	−1.80	0	0	NM	NM
38	250	50	2.0	−1.80	34	11	NM	NM
39	300	50	7.0	−1.80	69	40	NM	NM
40	300	50	2.0	−1.80	48	16	NM	NM
41	300	100	7.0	−1.80	51	21	NM	NM
42	300	100	2.0	−1.80	52	21	NM	NM
43	300	50	2.0	−1.80	61	36	22	9
44	300	50	2.0	−2.00	77	46	9	2
45	300	50	2.0	−2.00	63	38	NM	NM

NM: Not measured.

Table 7. Controlled current reduction of carbon dioxide at indium-impregnated, PTFE-bonded, carbon gas-diffusion electrodes

Electrode	*Curing temperature (°C)*	*pH*	*Applied current density* ($mA\,cm^{-2}$)	*Uncorrected cathode potential (V versus SCE)*	*Current efficiency formic acid (%)*	*Partial current density formic acid* ($mA\,cm^{-2}$)	*Current efficiency of exit gas (%)*	
							H_2	*CO*
46	250	2.0	50	−1.7 to −2.0	13	7	NM	NM
47	300	2.0	50	−1.5 to −1.8	37	18	NM	NM
48	300	2.0	50	−1.9 to −2.0	66	33	NM	NM
49	300	2.0	100	−2.4 to −2.5	87	87	12	7
50	300	2.0	100	−2.2	84	84	NM	NM
51	300	2.0	150	−2.4 to −2.5	53	80	NM	NM

Electrolyte: 50 $g\,l^{-1}$ Na_2SO_4. NM: Not measured.

under controlled current conditions (Table 7). Electrode 46, which had been cured at 250° C, demonstrated a poor current efficiency (13%) for formic acid when it was electrolysed at a current density of 50 mA cm^{-2}. Higher yields of formic acid were found with electrodes cured at 300° C (electrodes 47 to 51). Current efficiencies of 37 and 66% were recorded at those electrodes polarized at a current density of 50 mA cm^{-2} (electrodes 47 and 48, respectively). Surprisingly, higher figures were recorded at similar electrodes polarized at 100 mA cm^{-2} (electrodes 49 and 50), where the current efficiency for formic acid production was found to exceed 80%. Total current efficiency checks were carried out on electrode 49 giving 87% formic acid, 12% hydrogen and 7% carbon monoxide, a total of 104% which is an acceptable charge balance. The current efficiency for formic acid decreased to 53% at that electrode polarized at 150 mA cm^{-2} (electrode 51), corresponding to a partial current density for formic acid production of approximately 80 mA cm^{-2}.

Hydrogen evolution from the wet side of the electrode was evident to varying degrees at all the indium-impregnated electrodes evaluated under controlled current conditions.

3.5. *Tin-impregnated electrodes*

Current efficiencies for formic acid production of about 58% were recorded at two tin-impregnated electrodes polarized at a potential of -1.80 V in 50 g l^{-1} sodium sulphate acidified to pH 2 (electrodes 52 and 53, Table 8). The partial current densities for formic acid production were estimated to be 38 and 35 mA cm^{-2}, respectively. Analysis of the carbon dioxide exit stream during the electrolysis with electrode 52 revealed the presence of both hydrogen (current efficiency 12%) and some carbon monoxide (current efficiency 7%). Some hydrogen evolution was visible from the wet side of electrode 53.

The electrochemical reduction of carbon dioxide at tin-impregnated electrodes was also performed in sodium chloride electrolytes. A current efficiency for formate production of 49% with a partial current density of 26 mA cm^{-2} was obtained at an electrode polarized at -1.80 V in 50 g l^{-1} sodium chloride (electrode 54). Hydrogen (current efficiency 22%) and a small amount of carbon monoxide (current efficiency 4%) were present in the carbon dioxide exit stream. The current efficiency for formic acid decreased to 30% with a partial current density of 14 mA cm^{-2} when an electrode was polarized at -1.80 V in a sodium chloride electrolyte which had been acidified to pH 2 (electrode 55). The current efficiency for hydrogen production (from the dry side of the electrode) increased to 45%, whereas the amount of carbon monoxide produced was almost unchanged (current efficiency 5%).

4. Discussion

The low solubility of carbon dioxide in aqueous electrolytes limits the maximum current density possible for the reduction of carbon dioxide to formate at solid electrodes to, at the most, 1–2 mA cm^{-2} [2–12]. In addition, the rapid onset of excessive amounts of hydrogen evolution has

Table 8. Controlled potential reduction of carbon dioxide at tin-impregnated PTFE-bonded carbon gas diffusion electrodes (cured at 300° C)

Electrode	*Electrolyte*	*pH*	*Potential (V versus SCE)*	*Current efficiency formate (%)*	*Partial current density formate (mA cm^{-2})*	*Current efficiency of exit gas*	
						H_2	*CO*
52	50 g l^{-1} Na_2SO_4	2.0	-1.80	57	38	12	7
53	50 g l^{-1} Na_2SO_4	2.0	-1.80	58	35	NM	NM
54	50 g l^{-1} NaCl	7.0	-1.80	49	26	22	4
55	50 g l^{-1} NaCl	2.0	-1.80	30	14	45	5

NM: Not measured.

restricted the acidity of the electrolytes to pH values of not less than about 4. Thus the principal product reported in the literature has been the formate ion, not formic acid.

Our initial results obtained with the non-impregnated, carbon gas-diffusion electrodes were encouraging. Carbon dioxide could be reduced to formate at rates as good as, if not better than, those reported using a variety of solid electrodes [2–12]. However, hydrogen evolution remained the predominant reaction.

The incorporation of lead, a high hydrogen overvoltage electrocatalyst, resulted in an immediate and significant improvement in the electrode performance. Addition of 10 wt % lead increased the current efficiency for formate production from virtually zero to 40% at a partial current density of 16 mA cm^{-2}. Increasing the lead content of the electrode did not seem to enhance the rate of electroreduction of carbon dioxide to formate (electrodes 15 to 17, Table 2). However, doubling the electrode loading gave rise to at least a two-fold increase in the partial current density for formate production (see Table 2).

Micronizing the carbon support–water mixture produced a carbon–water slurry containing very small carbon particles, ideal as an electrocatalyst support material for PTFE-bonded, carbon gas-diffusion electrodes [16]. Lead-impregnated electrodes made from carbon slurries prepared in this manner proved to be highly efficient for reducing carbon dioxide to formate with current efficiencies of over 80% and partial current densities of about 30 mA cm^{-2}. More importantly, the results (Table 3) show that in the pH range 5.0 to about 1.5, formate production is the dominant reaction and that the rate of reduction of carbon dioxide is independent of pH. Calculations based on the pKa value of formic acid reveal that at pH 2.0, undissociated formic acid is the predominant species in solution. Thus the ability to reduce carbon dioxide at pH 2.0 offers the distinct advantage of producing formic acid directly. With more acidic solutions (pH < 1.5) hydrogen evolution dominates and the current efficiency for reduction of carbon dioxide decreases by 16-fold. For example, at pH 1.0 the partial current density for the reduction of carbon dioxide to formic acid dropped to about 5 mA cm^{-2}.

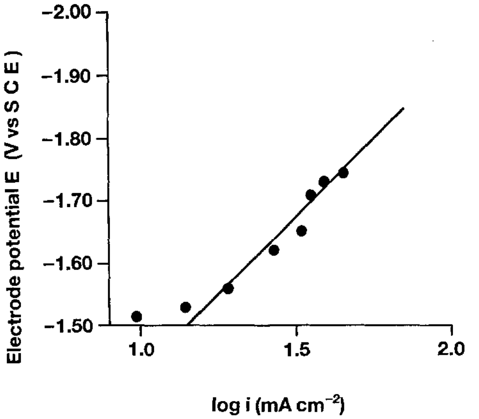

Fig. 2. Tafel plot for the reduction of carbon dioxide at a lead-impregnated, PTFE-bonded, carbon gas-diffusion electrode.

High rates of reduction of carbon dioxide were demonstrated at lead-impregnated electrodes operated at a current density of 115 mA cm^{-2} in electrolyte at pH 2, producing formic acid in virtually 100% current yield at an *iR*-corrected potential of approximately -1.8 V. Thus, we have been able to achieve, for the first time, the electrochemical reduction of carbon dioxide to formic acid at rates in excess of 100 mA cm^{-2} in aqueous solution at normal temperatures and pressures.

A striking feature noted in most of the experiments conducted in the controlled current mode was a sudden increase in the overvoltage of the cathode, the initial electrode potential being substantially less cathodic than its steady-state value, a value reached after about 2 min. Analysis of the catholyte confirmed that carbon dioxide was being reduced to formic acid during this period. A possible reason for this sudden increase in the electrode potential is discussed below.

The electrochemical reduction of carbon dioxide to formic acid is an irreversible reaction. Eyring and co-workers [3] have shown that the reaction proceeds with a large cathodic overpotential and exhibits Tafel slopes of over 200 mV per decade. Fig. 2 shows that the lead-impregnated electrodes reported in this work exhibit Tafel slopes of approximately 500 mV per decade. The figure shows a steady-state *i*–*E* plot for a lead-impregnated, gas-diffusion electrode polarized in $50\,\mathrm{g\,l^{-1}}$ sodium sulphate solution acidified to pH 2.0. Potentials corrected for *iR* were used and are plotted against the partial current density for the reduction of carbon dioxide to formic acid at a range of electrode potentials.

The reason for the high Tafel slope is not entirely clear. It may be that a non-conducting barrier is formed on the electrode surface, possibly as a result of the reaction between the electrogenerated carbon dioxide anion radical and the metallic lead (see [17] for an example of the reaction between lead electrodes and radicals). High Tafel slopes resulting from the formation of non-conducting barriers are well-documented in the literature. For example, Novak and Hough [18] and others [19, 20] reported Tafel slopes of over 500 mV per decade for fluorine evolution on graphite. Slopes of over 200 mV per decade were reported also for hydrogen evolution on cathodes covered by non-conducting barriers [21]. The formation of such a barrier on the electrode surface would also account for the sudden increase in the cathode potential observed during the controlled current electrolysis experiments and the reduction in current density during the controlled potential electrolyses.

High rates of reduction of carbon dioxide to formic acid were also recorded at gas-diffusion electrodes prepared using carbon impregnated with either indium or tin. An almost complete lack of activity was observed at those indium-impregnated electrodes which had been cured at either 140 or 250° C. However, excellent results were obtained with those electrodes which had been cured at 300° C. The form and distribution of the indium in these electrodes is not known, but these results indicate that no significant amount of reduction of the indium trichloride occurred until the curing temperature was higher than about 250° C.

In addition to formic acid, small quantities of carbon monoxide were produced at the indium- and tin-impregnated electrodes, a possible reduction product of carbon dioxide which was never observed using the lead-impregnated electrodes. Carbon dioxide has been reduced electrochemically to carbon monoxide in non-aqueous solvents at mercury cathodes [22, 23]. Amatore and Savéant have discussed a possible mechanism for this reaction [24]. They proposed that carbon monoxide was formed via a reaction between carbon dioxide radical anion and unreacted carbon dioxide. It is not known if a similar reaction sequence occurs at these indium- and tin-impregnated electrodes.

Hydrogen evolution occurred from both the gas and electrolyte sides of most of the indium- and tin-impregnated, gas-diffusion electrodes. As no attempt was made to measure the amount of gases which evolved from the wet side of these electrodes, the charge balances for the reduction of carbon dioxide presented in Tables 6, 7 and 8 are less than 100%.

Comparison of the results presented in this paper shows that the performance of the indium- and tin-impregnated electrodes is lower than that achieved by those containing lead. Under comparable electrolysis conditions (controlled potential electrolysis at -1.8 V, electrolyte pH 2), the partial current densities recorded at the lead-, indium- and tin-impregnated electrodes were 26, 36 and $35\,\mathrm{mA\,cm^{-2}}$, respectively. However, the electrolysis at the latter two electrodes was less selective, formic acid production being accompanied by a side reaction yielding carbon monoxide and by incomplete suppression of the hydrogen evolution reaction. As already noted above, the current efficiency for formic acid at lead-impregnated electrodes did not decrease as either the electrode potential or the applied current density was increased, partial current densities of greater than $100\,\mathrm{mA\,cm^{-2}}$ being readily obtained.

The electrochemical reduction of carbon dioxide to industrially useful compounds has been a long-term goal of many electrochemists (see [25] for a recent review). Previous attempts have been restricted by the relatively low current densities which are achieved using solid electrodes [1 – 12]. The results presented in this paper are the first reports of the electrochemical reduction of carbon dioxide at high (i.e. greater than $50\,\mathrm{mA\,cm^{-2}}$) current densities. Unfortunately, all the electrodes prepared in this investigation demonstrated high Tafel slopes and exhibited high overpotentials for this reaction. It would be necessary to develop electrodes which reduced carbon dioxide to formic acid with much smaller Tafel slopes and overpotentials before this electrochemical route to formic acid could become economically viable.

5. Conclusions

The results presented in this paper demonstrate, for the first time, that carbon dioxide can be reduced to formic acid at current densities in excess of $100\,\mathrm{mA\,cm^{-2}}$ using lead-impregnated, PTFE-bonded gas-diffusion electrodes. The high-rate electroreduction was performed at room temperature and atmospheric pressures in acidic aqueous electrolytes (pH 2.0). However, the cathodic overpotential for the reduction of carbon dioxide to formic acid is large ($> 1.3\,\mathrm{V}$) and the reaction exhibits high Tafel slopes, possibly due to the formation of non-conducting barriers on the electrode surface.

The activity of the electrodes impregnated with indium appeared to be similar to those prepared with tin, but lower than those containing lead. In addition to formic acid, small quantities of carbon monoxide were produced at the indium- and tin-impregnated electrodes.

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