

# REDUCTION OF CARBON DIOXIDE TO FORMIC ACID IN A SOLID POLYMER ELECTROLYTE (SPE) REACTOR

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## Abstract.

The aim of the research was to develop an inherently clean and selective process for the electrocatalytic reduction of carbon dioxide to formic acid. The research evaluated electrocatalytic metalised (In, Pd, Pb, Pt, Pt/Ru, Cu) graphites for the reduction of carbon dioxide and unsupported metal deposited SPE electrode structures, using a range of membrane materials as alternatives to Nafion<sup>R</sup>, including fluorinated anion exchange membranes. Good yields of formic acid were produced with all catalysts, except Pt and Pt/Ru.

## Introduction

Carbon dioxide is an abundant carbon source for the manufacture of alcohols, aldehydes, carboxylic acids, etc. and has thus stimulated interest in its reduction. The electroreduction of CO<sub>2</sub> has been the subject of considerable research and has been extensively reviewed, e.g.[1]. In aqueous electrolytes, the reduction of CO<sub>2</sub> to formate is favoured on selected cathode materials (e.g. Sn, Pb, In, Pd). The use of aqueous electrolytes has several limitations such as, low solubility in aqueous solutions, and resultant low operating current densities, and separation of the formate from the aqueous electrolyte will be expensive. The alternative use of non-aqueous solvents, although increasing carbon dioxide solubility, brings problems associated with the handling and recovery of the material. To overcome these limitations we carried out the reduction in the gas/vapour phase using a solid polymer electrolyte membrane.

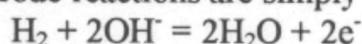
## Experimental Research Programme

Electrode membrane assemblies (EMA), shown schematically in Fig 1, studied in this work were typically made in the following manner. The anode consisted of a Teflonised carbon cloth support (E-Tek, type 'A'), of 0.35 mm thickness, upon which was spread a thin layer of uncatylsed (ketjenblack 600) carbon, bound with 10 wt% Nafion<sup>®</sup> from a solution of 5 wt.% Nafion<sup>®</sup> dissolved in a mixture of water and lower aliphatic alcohol's (Aldrich). The catalysed layer, metal catalyst (typical 2 mg cm<sup>-2</sup> metal loading) and bound with 10 wt% Nafion<sup>®</sup>, was spread on this diffusion backing layer. The EMA was obtained by hot pressing the anode and cathode on either side of the pre-treated membrane. The anode material used platinum supported carbon electrodes, constructed using the same method as for the cathode.

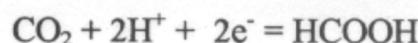
Tests were performed with a cell (Fig. 1), with a cross-sectional area of 9 cm<sup>2</sup>, fitted with one electrode assembly (EMA) sandwiched between two graphite blocks which had a flow bed, parallel channels, cut out for carbon dioxide or hydrogen flow. The anode reaction was either the evolution of oxygen or the oxidation of hydrogen gas. Products from the cathode the anode stream were collected in cold traps and analysed by GLC.

## Results and Discussion.

The two electrode reactions are simply written as



or



The two combinations of reactions represent operation in, either an alkaline environment (A) or an acid environment (B). In the former case the SPE will be an anion conductor whilst in the latter case a weak acid conductor.

The focus of this research was evaluation of SPE electrodes in terms of electrochemical response and product yield. All the cathode catalysts used produced respectable current yields of formic acid, except Pt and Pt/Ru alloy. Indium in particular produced yields up to 100% under specific conditions of operation, e.g. potential and current density, as shown in Fig. 2. The use of an anion exchange membrane was found to be an effective alternative approach to proton conducting membranes, giving yields greater than 80%. One of the major byproducts of the cathode reaction is hydrogen gas. The attraction of the SPE approach is that this gas can be fed to the anode chamber, after recovery of product, by condensation, and used to reduce the cell voltage.

[1] M Jitaru, D A Lowry, M Toma, B C Toma, L Oniciu. J. Appl. Electrochem. 27 (1997) 875.

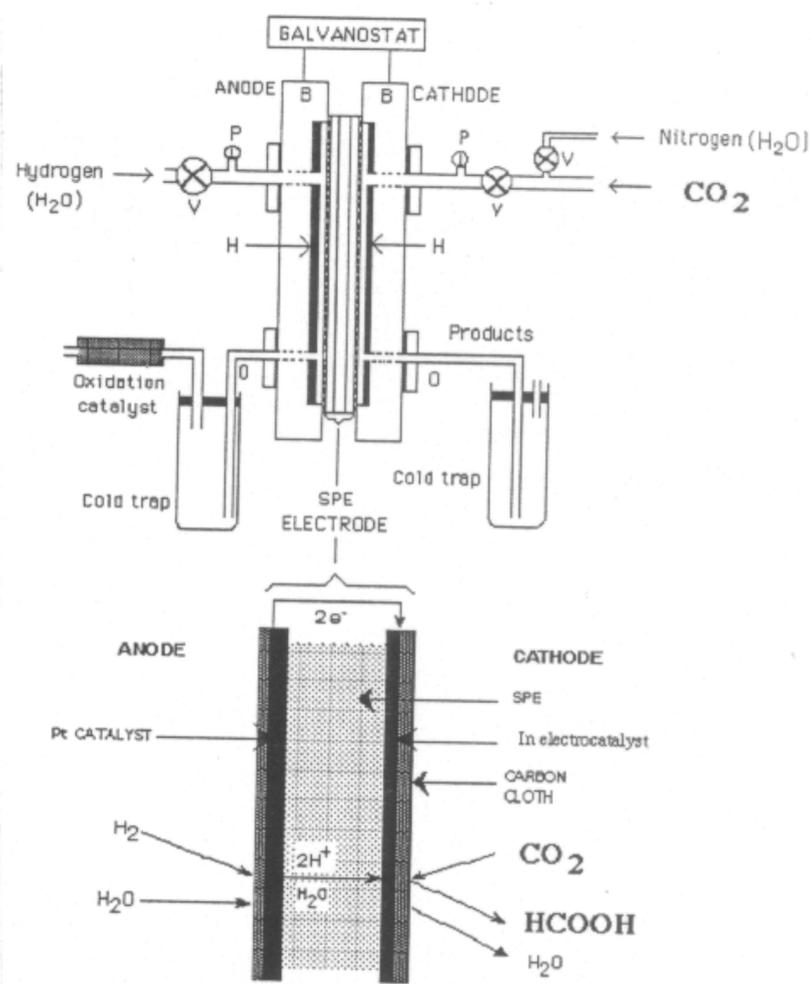


Fig. 1 Schematic of Cell and Flow circuit

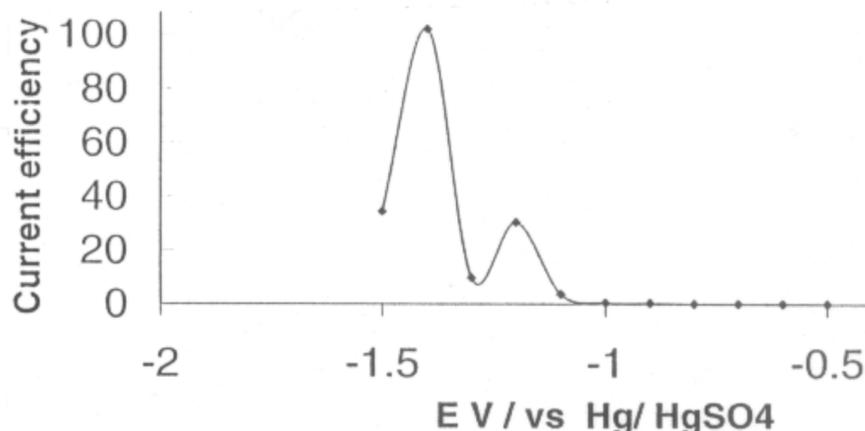


Fig. 2. Current efficiency for formic acid at Indium bonded electrodes.

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