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Electrochemical membrane reactor for the reduction of carbon dioxide to formate

K. SUBRAMANIAN[1,*], K. ASOKAN[1], D. JEEVARATHINAM[2] and M. CHANDRASEKARAN[1]
[1]*Central Electrochemical Research Institute (CSIR), Karaikudi 630 006, India*
[2]*Indian Institute of Technology, Delhi, India*
*(*author for correspondence, e-mail: sivas_tsia@cecri.res.in)*

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Abstract

An electrochemical reactor with anode and cathode chambers separated by a composite perfluoro polymer cation exchange membrane was designed, fabricated and used for the reduction of dissolved carbon dioxide under ambient conditions to formate. The flow reactor enhanced the mass transfer of carbon dioxide compared to the batch reactor and maximum current efficiency of 93% for formate formation was obtained. A formate concentration of 1.5×10^{-2} mol dm^{-3} was obtained. Experiments were conducted using two different perfluoro polymer membranes – Nafion 961 and Nafion 430. Optimum values of flow rate and current density were evaluated for the energy efficient formation of formate in aqueous phosphate buffer solutions.

1. Introduction

Carbon dioxide is easily available in nature and huge amounts are generated by human activities; it is a practically infinite carbon source for the chemical industry for the manufacturing of alcohols (methanol and ethanol), aldehydes, hydrocarbons (methane and ethylene) and carboxylic acids (formic and oxalic acids). Reactive use of CO_2 is limited by the fact that it is very stable and energy must be supplied to drive most transformations. When compared to chemical methods, electrochemical methods are less cumbersome for the removal of CO_2 from the atmosphere and converting it into more valuable chemicals [1, 2]. No large-scale process is currently available for the electro reduction of CO_2.

There is a growing demand for formic acid. The use of formic acid starts from the traditional pickling of leather to highly advanced pharmaceutical syntheses. Of late, it is being used in paper and pulp production and this process produces fully bleached chemical pulp from both hardwood and softwood without sulphur or chlorine chemicals. World consumption of formic acid was approximately 0.44 million tonnes in 2003. Significant amounts of formic acid are produced as a byproduct in the manufacture of other chemicals, especially acetic acid. When methanol and carbon monoxide are combined in the presence of a strong base, the formic acid derivative, methyl formate results and on hydrolysis of methyl formate, formic acid is produced. These processes are neither straightforward nor environment friendly.

Formate can be produced electrochemically [3–7] with a higher selectivity than other end products. Chaplin and Wragg [8] reviewed the studies of all aspects of electrochemical formation of formate. Studies on the performance of a flow reactor with perfluoro sulphonic acid membrane for electroreduction of CO_2 to formate were carried out by Osamu Hamamoto et al. [9]. They claimed to have developed a process based on these studies [10]. They operated a flow reactor with Nafion 117 ion-exchange membrane separating the CO_2 reduction reaction on a glass fibre reinforced lead wire cathode (1 cm^2 area) and the sulphite oxidation reaction on a carbon fibre anode (10 cm^2 area). They observed a current efficiency near to 100% at a constant applied cell voltage of 1.4 V with CO_2 absorbed phosphate buffer solutions (pH 6) in the catholyte. The apparent current density for CO_2 reduction was 2 mA cm^{-2}.

The present studies aim at the development of an energy efficient electrochemical route for the production of formate by the reduction of CO_2. We have designed and fabricated a filter press type flow reactor for CO_2 reduction to form formate at constant current density. The use of a *perfluoro polymer membrane* helps to maintain alkaline conditions in the anode chamber to ensure oxygen formation at low equilibrium potentials. The electroreduction of carbon dioxide requires high hydrogen overvoltage to obtain formate with high current efficiencies. Lead cathodes [11, 12] have well proven efficiency for CO_2 reduction. Lower oxygen overvoltage and good stability of IrO_2/Ta_2O_5 films [13–15] have been widely established. A lead plated

stainless steel woven mesh cathode and a IrO_2/Ta_2O_5 film coated on expanded titanium mesh anode were used in the present study.

2. Experimental details

2.1. *Electrodes*

2.1.1. *Lead cathode*

Stainless steel (SS 316) woven wire mesh (wire diameter 0.2 mm) was chosen as the substrate. A geometrical area of 9×5 cm^2 of the substrate metal was degreased washed well with water and etched in hydrofluoric acid for few minutes. The etched strip was then immersed in lead fluoborate bath containing: lead fluoborate 140 g dm^{-3}, free fluoboric acid 40 g dm^{-3}, boric acid 15 g dm^{-3}, lignin sulphonic acid 2 g dm^{-3} and cumarine 1 g dm^{-3}. A constant current of 40 mA cm^{-2} was passed through the system for 1 h. This produced a fine deposit of lead over the SS substrate.

2.1.2. *IrO_2/Ta_2O_5 anode*

This was prepared by applying a thin layer of a solution containing $IrCl_3$ and $TaCl_5$ dissolved in isopropanol, on pretreated flattened expanded titanium mesh of geometrical area 9×5 cm^2 and firing at 723 K in a preheated furnace. The process was repeated until a coating thickness of 5–6 μm of IrO_2/Ta_2O_5 was achieved.

2.2. *Membrane*

The anode and cathode were separated by a cation exchange perfluoro polymer membrane. Two different Dupont membranes *Nafion* 961 and *Nafion 430* were used. The Nafion 961 membrane has a thick (100 μm) perfluorosulphonic acid polymer layer on one side of the thin PTFE fibre woven matrix, while the other side has a thin (10 μm) of perfluorocarboxylic acid polymer layer. The Nafion 430 membrane has only a perfluorosulphonic acid polymer layer on the thin PTFE fibre woven matrix.

2.3. *Reactor assembly*

The anodic and cathodic chambers were made from solid polypropylene materials. The anode and cathode chambers had dimensions of $9 \times 5 \times 1$ cm^3. The chambers were fabricated by carving out a cavity of dimensions $9 \times 5 \times 1$ cm^3 at the centre of the polypropylene block of dimensions $13 \times 9 \times 2.2$ cm^3. The cathode and anode chambers had provisions for electrolyte inlet and outlet. Dupont cation exchange membrane, *Nafion 961*/*Nafion 430* was placed between the anode and cathode chambers. The reactor assembly was made airtight and leak proof by placing EPDM gaskets between the chambers and the membrane. When using Nafion 961 membrane, it was placed in such a way that the carboxylic acid layer faced the anode and the sulphonic acid layer faced the cathode. The anode and cathode chambers were arranged in such a way that the anolyte and catholyte flows were in countercurrent directions. The gap between the electrodes and membrane was kept at 3 mm. The reactor stack was held tightly in place using two mild steel backing plates with stainless bolts and nuts.

2.4. *Electro reduction of CO_2*

All the substances were analytical-reagent grade and all solutions were prepared using triply distilled water. The experiments were carried out at 298 ± 1 K. Carbon dioxide was absorbed at atmospheric pressure in potassium phosphate buffer solution (0.2 M $K_2HPO_4 + H_3PO_4$, pH 7) in a vertical absorption column. The amount of gas absorbed was determined by volumetric analysis. The CO_2 absorbed solution was fed to the cathode chamber. About 0. 2 M KOH solution was fed to the anode chamber to form oxygen. The amount of formate formed was determined by high pressure liquid chromatography (HPLC – Shimadzu, Japan) and values were counter checked by the bromometric method [16]. DC current (*Aplab*-constant current regulator, 0–1 A, 0–35 V) was applied to the reactor and cell voltage was recorded at regular intervals. Peristaltic pumps were used to maintain the feed flow rate to the electrode chambers. The effect of electrolyte flow rate and applied current density on the current efficiency for formate production was studied for an operating time of 1 h.

2.5. *Experimental set-up*

Figure 1 shows a block diagram of the experimental set-up. Two separate overhead tanks of capacity one litre were mounted at an elevation to provide the necessary head for the flow of feed to the reactor. The hold up volume of each chamber was 30 ml. As the flow rates are very small, two peristaltic pumps were employed, one for feeding anolyte and catholyte into the electrode chambers. The effluent from the cathode chamber was collected and analyzed. The exit stream from the anode chamber was collected and analysed for KOH depletion.

3. Principle of membrane cell process for electrochemical reduction of CO_2

The cation exchange membrane used, selectively allows the transport of K^+ ions from the anode chamber to the cathode chamber along with associated water molecules. It suppresses the back migration of $HCOO^-$ ions from

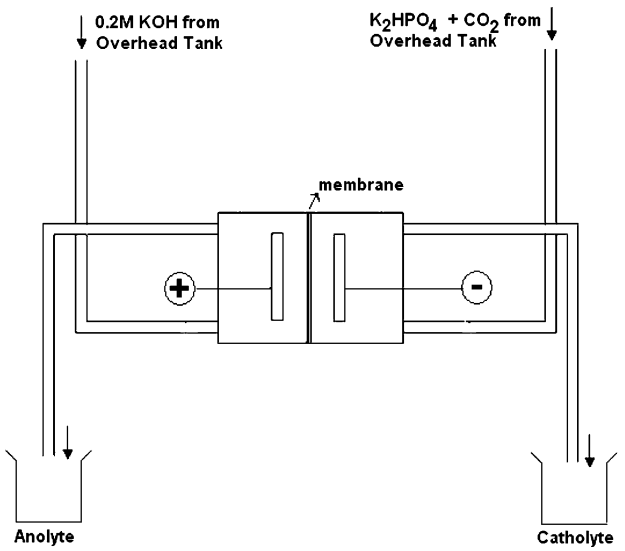

Fig. 1. Flow reactor for electrochemical reduction of carbon dioxide to formate.

the cathode to anode chamber. The predominant reaction occurring in the anode chamber (pH 14) is oxygen evolution.

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e$$
$$E_O = +0.40 \text{ V vs NHE}$$

The main reaction [17] occurring in the cathode chamber (pH 7) is the formation of formate ions.

$$CO_2 + H_2O + 2e \rightarrow HCOO^- + OH^-$$
$$E_o = -0.61 \text{ V vs NHE}$$

Formate ions combine with potassium ions transported through the membrane from the anode chamber to form potassium formate. The overall equilibrium cell voltage is −1.01 V.

The principle of the process is illustrated in Figure 2. Competing reactions, namely H_2 evolution and CO formation [17] affect the efficiency of the reactor to a significant extent.

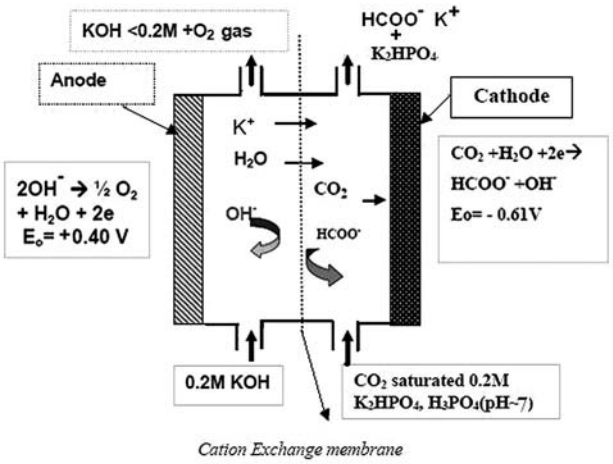

Fig. 2. Membrane reactor for electrochemical reduction of CO_2 to formate.

$$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O$$
$$E_o = -0.109 \text{ V vs NHE}$$
$$2H_2O + 2e \rightarrow 2OH^- + H_2$$
$$E^o = -0.109 \text{ V vs NHE}$$

4. Results and discussion

CO_2 was electrochemically reduced to formate at the cathode in aqueous solutions. The solubility of CO_2 in aqueous solutions is of the order of 30 mM at 298 K. Hence, mass transfer of CO_2 is a problem. In this context, a flow reactor is more efficient for the electro reduction of CO_2 to formic acid. In a flow reactor, the catholyte containing dissolved CO_2 fed to the reactor is electrochemically reduced and flows out continuously in the form of formate.

The variation of formate content in the cathode chamber effluent as a function of flow rate is shown in Figure 3. Figure 4 shows the effect of catholyte feed rate on the current efficiency for formate production. From Figures 3 and 4, it is observed that current efficiency as well as amount of formate produced increase with the flow rate and reach maximum values at a flow rate of 3.2 ml min^{-1}, thereafter both the values of current efficiency and amount of formate decrease with increase in flow rate. Increase in flow rate effects an increase in mass transfer of CO_2 to the electrode surface, leading to an increase in the concentration of CO_2 available for reaction, producing more formate. But after reaching a flow rate of 3.2 ml min^{-1}, current efficiency as well as amount of formate formation start decreasing. This may be due to the shorter residence time at higher flow rates or excessive turbulence in the cathode chamber affecting the absorption of CO_2 molecules on to the active sites or the production of dead zones across part of the cathode. Some of the CO_2 molecules entering the reactor leave without undergoing electrochemical reaction, leading to a low yield of formate at high flow rates.

The effect of current density on current efficiency was studied at a constant flow rate of 3.2 ml min^{-1} (Figure 5). As the current density increases the current efficiency increases and reaches a maximum value of 93%, at a current density of 2 mA cm^{-2} and then it starts decreasing rapidly. As current density increases, hydrogen evolution becomes the more dominant reaction than the reduction of carbon dioxide. The effect of current density on concentration of formate formed was studied at a constant flow rate of 3.2 ml min^{-1} (Figure 6). The concentration of formate increases steeply with current density and reaches a maximum value, (0.01596 mol dm^{-3}) and decreases rapidly. As the current density increases, the rate of formation increases and at above 2 mA cm^{-2}, the mass transfer

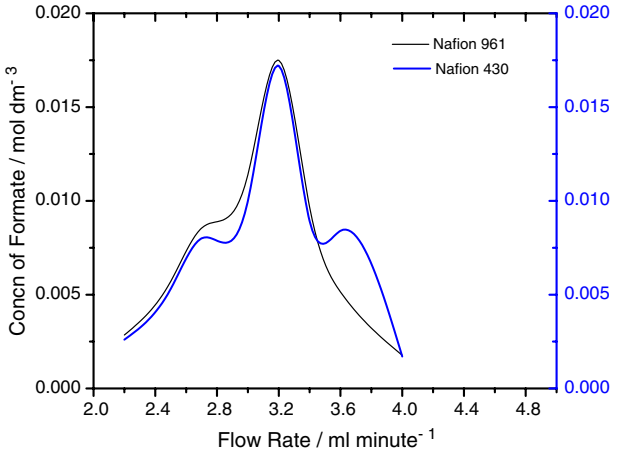

Fig. 3. Variation of amount of formate formed with respect to the flow rate of catholyte feed, current density: 2 mA cm^{-2}, *T*: 298 K, charge: 0. 1 Ah.

rate affects the formate formation reaction. This phenomenon is also one of the indicators that electroreduction of carbon dioxide is mass transfer controlled, due to the low solubility of carbon dioxide, in aqueous solutions. The trends observed seem to be more or less the same for both membranes as they play only the role of a separator (Figure 7).

4.1. *Mass transfer coefficient*

The electrochemical reactor consists of two parallel electrodes of definite width. Under laminar flow conditions, the mass transfer coefficient can be determined using the empirical relation, $Sh = 1.467\ [2/(1+\gamma)]^{1/3}\ (Pe \times d_e/L)^{1/3}$ [18], where, *Sh* is the Sherwood number $= k_c\ d_e\ /D$, k_c the mass transfer coefficient, d_e the equivalent diameter, *D* the diffusivity of the species in the medium, γ the ratio of distance between the electrodes (thickness of the membrane, i.e., 1.2 mm) to the width of the electrode, *Pe* the Peclet number = (Reynolds number × Schmidt number), *L* the length of the electrode.

Reynolds number, $Re = d_e\ u\ \rho/\mu$, where d_e is the diameter in m, *u* the velocity in m s^{-1}, ρ the density of the medium in kg m^{-3}, μ the viscosity of the medium in kg $m^{-1}\ s^{-1}$.

Equivalent diameter $= 2(w \times b)/(1+b) = 0.007$ m.

Velocity of flow, u = flow rate/area $= 0.0011$ m s^{-1}.

$\rho = 1000\ kg\ m^3$; $\mu = 0.001\ kg\ m^{-1}\ s^{-1}$

Reynolds number,

$Re = 0.007 \times 0.00011 \times 1000/0.001 = 0.77$,

Schmidt number, $Sc = \mu/D\rho$; $D = 10^{-9}\ m^2\ s^{-1}$

$Sc = 0.001/(10^{-9} \times 1000) = 1000$; $\gamma = 0.12$

Sherwood number,

$Sh = 1.467\ [2/(1+0.12)]^{1/3}$

$[0.77 \times 1000 \times (0.007/0.09)]^{1/3} = 6.86.$

Mass transfer coefficient,

$k_c = Sh \times D/d_e = 6.86 \times 10^{-9}/0.007 = 9.8 \times 10^{-7}\ ms^{-1}$.

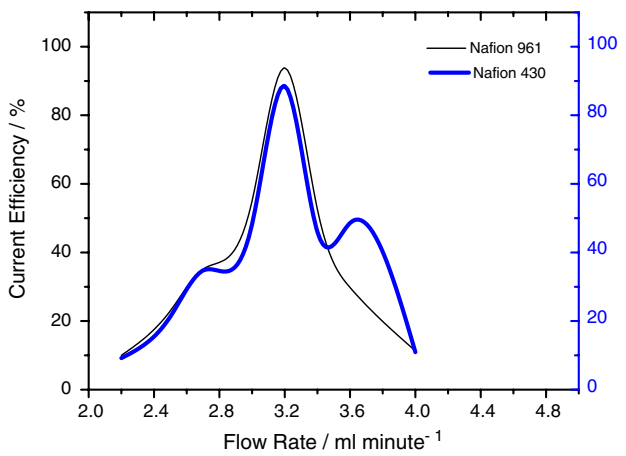

Fig. 4. Variation of current efficiency with respect to the flow rate of phosphate buffer (CO_2 absorbed) catholyte feed, current density: 2 mA cm^{-2}, *T*: 298 K, charge: 0.1 Ah.

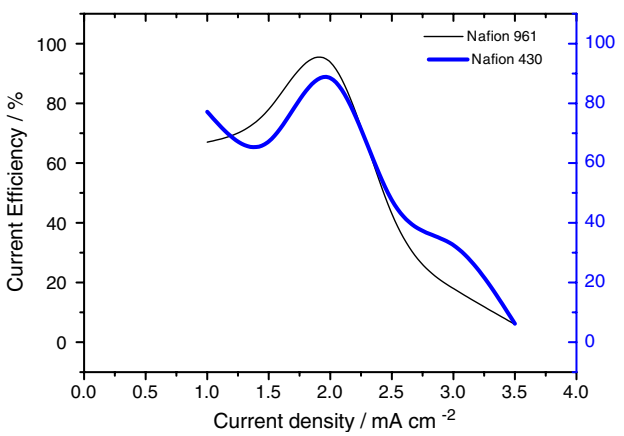

Fig. 5. Effect of current density on current efficiency at 3.2 ml min^{-1} flow rate of phosphate buffer (CO_2 absorbed) catholyte feed, current density: 2 mA cm^{-2}, *T*: 298 K, duration of passage of current: 1 h.

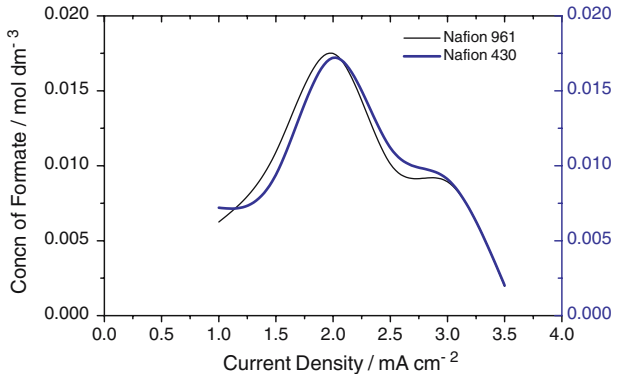

Fig. 6. Effect of current density on the formate concentration at 3.2 ml min^{-1} flow rate of phosphate buffer (CO_2 absorbed) catholyte feed, current density: 2 mA cm^{-2}, *T*: 298 K, duration of passage of current: 1 h.

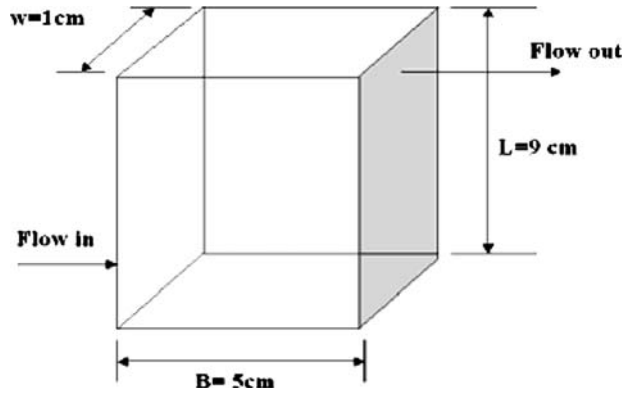

Fig. 7. Sectional view of electrode chamber.

The cell voltage was measured at a constant current density (2 mA cm^{-2}) with time (Figure 8). Cell voltage initially increases, reaches a stable value, remains at the steady value for most of the experiment and increases again towards the end. Cell voltage is the sum of equilibrium electrode potentials, overpotential and potential drop across the electrolytes and membrane. Since the current density is very low in this system, the cell voltage observed is directly proportional to carbon dioxide reduction and oxygen evolution overpotential. Cell voltage is a stronger function of ohmic drops (linear) than over potentials (logarithmic). The cell voltage is high for the Nafion 430 membrane, because of the higher IR drop across the thicker separator.

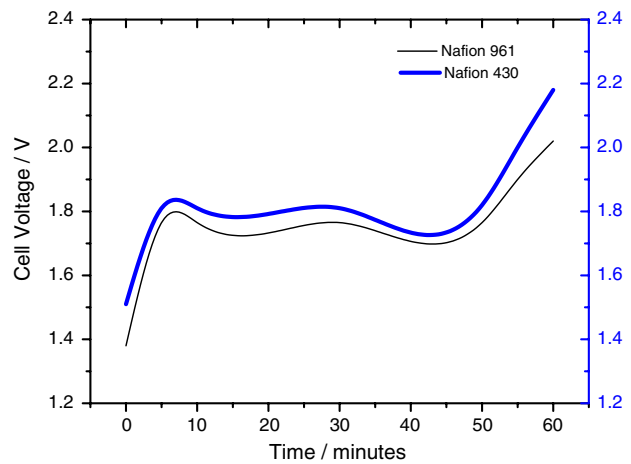

Fig. 8. Variation of cell voltage with time for carbon dioxide reduction in phosphate buffer solutions and oxugen evolution in alkaline solution (0. 2 M KOH). Current density: 2 mA cm^{-2}, duration of electrolysis: 1 h, *T*: 298 K.

5. Conclusions

A flow type electrochemical membrane reactor for reduction of CO_2 was operated with a composite perfluorosulphonic-carboxylic group ion-exchange membrane, lead coated cathode and IrO_2/Ta_2O_5 film anode. The reaction products in the cathode and anode chambers are formate and oxygen respectively. The reactor was operated at different current densities and catholyte feed rates and corresponding values of formate concentration, current efficiency and cell voltage were recorded. Process parameters for a membrane reactor of apparent electrode area of 45 cm^2 were evaluated. A maximum current efficiency of 93% was achieved for formate production (1.5×10^{-2} mol dm^{-3}) at an optimum flow rate 3.2 ml min^{-1} at 298 K. Under the above conditions, a cell voltage ranging from 1.4 to 1.7 V was observed at 2 mA cm^{-2} compared to the theoretical cell voltage of 1.01 V. It is proposed to extend the present studies to multiple monopolar reactors of similar design with improved cathode catalysts which is expected to improve the efficiency of formate production.

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