Journal of CO_2 Utilization 3–4 (2013) 49–55

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Effect of cationic and anionic solid polymer electrolyte on direct electrochemical reduction of gaseous CO_2 to fuel

L.M. Aeshala, R.G. Uppaluri, A. Verma *

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

ARTICLE INFO

Article history:
Received 10 August 2013
Received in revised form 5 September 2013
Accepted 8 September 2013
Available online 8 October 2013

Keywords:
Electrochemical reduction
Carbon dioxide
Faradaic efficiency
Hydrocarbons
Solid polymer electrolyte

ABSTRACT

The electrochemical reduction of carbon dioxide in the gaseous phase was investigated using cationic and anionic solid polymer electrolytes. Influence of solid polymer electrolyte medium on electrochemical reduction of gaseous CO_2 into fuel is studied. The electrodeposited Cu_2O on porous carbon paper was used as cathode whereas Pt/C on the carbon paper was used as anode. The products formed after the electrochemical reduction of carbon dioxide were analyzed by gas chromatography and high performance liquid chromatography. Experiments were carried out at room temperature and atmospheric pressure. Mainly methane, ethylene, and methanol were formed as products apart from the undesired hydrogen gas as a by-product. It has been found that anionic solid electrolyte was more favorable than cationic solid electrolyte. Faradaic efficiency for the conversion of CO_2 into products was more than 45% using anionic solid polymer membrane at 2.5 V and 5.4 mA cm^{-2}.

1. Introduction

Carbon dioxide is widely accepted as one of the main contributors to global warming [1] and there is need for methods to sequester it [2]. Various methods are being studied to recycle carbon dioxide to value added products such as methanol or dimethyl ether as a renewable source for efficient transportation fuel [3]. The electrochemical reduction of carbon dioxide (ERC) is a technique of particular interest since it may mitigate as well as utilize the CO_2 as a carbon source for the generation of value added products including fuel. Moreover, the synthesis of fuel by the conversion of CO_2 is of special interest for the storage of renewable energy, which may be supplied to the thermodynamically unfavorable CO_2 reduction reaction [4,5]. It has been reported that formation of anion radical (CO_2^-) is the rate determining step for the reduction of CO_2. The electrical potential for CO_2/CO_2^- is −1.9 V vs. NHE through single electron pathway. However, the requirement of this much high energy may be reduced by proton assisted multi-electron reduction of CO_2 [6,7]. A few of the representative proton assisted reactions* (Eqs. (1) and (2)) showing electrochemical reduction of carbon dioxide is given below,

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^0 = -0.38\,V \tag{1}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad E^0 = -0.24\,V \tag{2}$$

(*Above reactions are in aqueous acidic solution; E^0 is the standard potential with respect to NHE at 25 °C and 1 atmosphere pressure.)

The advantage of electrochemical reduction of CO_2 is that the water can be used as proton source. However, it is well known that the hydrogen evolution reaction (HER) is competitive to CO_2 electroreduction in the presence of aqueous electrolyte solution. The electrochemical reduction of carbon dioxide in aqueous solutions has been reported by many authors [8–11]. Nevertheless, the aqueous electrolyte has many disadvantages such as high ohmic loss, possibility of leakage from the reactor, increased HER, and mass transfer limitation of the solubilized CO_2 from bulk electrolyte to electrode surface. To tackle the problems, concept of solid polymer electrolyte (SPE) may be used. The use of SPE may have many advantages in comparison with liquid electrolytes, such as (i) good tensile strength; (ii) ease of handling, which allow the fabrication of thin films and thus low resistance; (iii) low convection, which reduces the problems of electrode erosion and increases the electrode life; and (iv) easy separation of the reaction products, etc. Though a many literatures shows the use of SPE but the SPE was used to separate anolyte from the aqueous catholyte in divided H-type cells [12–14]. A couple of literatures reported the use of SPE in flow type cells, in which CO_2 was sent to reactor in gas phase [15–18] or liquid phase (CO_2 saturated electrolyte solution) [19,20].

The investigators used Cu coated SPE using electro-less plating technique. When nafion was used as a cation exchange SPE, the ERC produced C_2H_4 as major product [15,16], whereas the use of selemion as anion exchange SPE produced CO and HCOOH as major products [17]. Nishimura et al. [21] conducted the gas phase ERC

* Corresponding author. Tel.: +91 361 2582255; fax: +91 361 2582291.
E-mail addresses: anil.verma@iitg.ernet.in, anil.verma@iitg.ac.in (A. Verma).

2212-9820/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jcou.2013.09.004

using selemion as an anionic SPE and Au as cathode catalyst. The electrochemical system produced only CO as a major product with a current efficiency of 90%. Machunda et al. [22] carried out electrochemical reduction of gas phase CO_2 using nafion membrane on electrodeposited Pb on GDE. It was observed that prior to the experiments, microstructure of the deposited Pb catalyst changed from grain-like to needle-like structure due to the exposure of humidified CO_2. Thus the needle-like structures provided high surface area for the reaction as supported by the increased current density during the initial stage of reduction process. Formic acid was formed selectively at −2 V with a maximum Faradaic efficiency of 65%. Delacourt et al. [23] developed an electrolysis cell design for the electrochemical reduction of CO_2 and H_2O to synthesize syngas (CO + H_2) at room temperature. They represented several cell designs based on polymer exchange membranes. The most effective design had configuration with a buffer layer of $KHCO_3$ in between cathode and nafion membrane. This allowed much greater efficiency for reduction of CO_2 to CO and achieved CO:H_2 in 1:2 ratio at −1.8 V NHE with a current density of 80 mA cm^{-2}. The ERC may also produce long chain hydrocarbons using gas phase conversion of carbon dioxide at room temperature and ambient pressure using Pt nanoparticles on carbon based electrode along with nafion membrane as SPE [24]. Narayanan et al. [25] studied the continuous ERC to formate in a polymer electrolyte membrane cell using Pb or In as catalyst and AMI-7001 or nafion in Na^+ form as SPEs. Formate was selectively formed for both the combinations using CO_2 saturated in bicarbonate or carbonate or pure water. However, the maximum Faradaic efficiency of 80% was achieved for formate with reduced hydrogen evolution when bicarbonate solution saturated with CO_2 was used. It was found that the Faradaic efficiency was strongly dependent on the concentrations of carbon dioxide, bicarbonate, and carbonate at the electrode surface. It was also observed that mass transport limitations can be mitigated and high efficiencies can be realized by conducting the electrolysis in pulse mode. Scott et al. [26] investigated various electrodes (Pb, Pd, In, Cu) for the selective formation of formic acid using cation and anion exchange membranes. It is reported that the formic acid yield was 80% more for anion exchange SPE as compared to cation exchange SPE. Recently, some preliminary studies have been shown for gas phase CO_2 electroreduction using various SPEs using Cu electrocatalyst [27]. Mainly formic acid, formaldehyde, carbon monoxide and methane were evolved with very low Faradaic efficiency.

It is found that the research work on SPEs is scanty. Only a few of the literatures are available, which reports the use of various SPEs along with different electrocatalysts for the product formation. However, there is hardly any literature, which reports explicitly the influence of anionic or cationic solid polymer electrolyte on the electrochemical reduction of carbon dioxide. Therefore, this research work is conducted to evaluate the role of cationic and anionic SPEs in the direct electrochemical reduction of gaseous carbon dioxide (dERC). In order to study the effect of cationic and anionic SPEs, two SPEs with similar backbone structures but different functional groups were chosen for the dERC study. The dERC was conducted under pulse mode electrolysis using similar operating conditions and electrocatalyst. Moreover, next section shows the thermodynamics of a representative electrochemical reaction in electrolyte medium.

2. Thermodynamics of dERC in electrolyte

In order to understand and explore the influence of electrolyte, thermodynamic efficiencies of various dERC products were calculated. Table 1 shows electrochemical reactions for a representative reaction product (CH_4) of dERC in cationic and anionic electrolytes where the standard electrode potentials were calculated using formation energies [28]. The corresponding thermodynamic data pertaining to CH_4 is shown in Table 2. Electrical energy (*EE*) is calculated using Gibbs free energy ($\Delta G^0 = nFE^0_{cell}$), where *n* is number of moles of electrons per mole of CO_2 consumed and *F* is the Faraday constant.

Table 1
Electrochemical reduction reactions of CO_2 for the formation of CH_4 in cationic and anionic electrolytes.

Electrolyte	Electrochemical reactions	Potential (E^0, V vs. SHE)
Cationic		
Cathode	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+0.17
Anode	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	−1.23
Overall	$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	−1.06
Anionic		
Cathode	$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$	−0.66
Anode	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	−0.4
Overall	$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	−1.06

The surplus thermodynamic efficiency for the formation of methane from CO_2 in the cationic and anionic electrolyte is shown in Table 2. However, the actual energy efficiency would be quite different than the thermodynamic efficiency and it can be calculated by thermodynamic efficiency and Faradaic efficiency.

3. Experimental

3.1. Materials

Pt/C (40 wt%) was purchased from Electro-Chem., USA. CMI-7000 and AMI-7001 were procured from Membrane International Inc., USA. Porous carbon paper (TGP-H-120) from Torayca was used as backing layer for electrode preparation. Other chemicals like H_2SO_4, and KOH were procured from Merck, India. All the chemicals were used without further purification unless specified and de-ionized water was used in all the experiments.

3.2. Method

3.2.1. Treatment of SPE

The procured CMI-7000 and AMI-7001 SPEs were treated prior to the use. The SPEs (CMI-7000 and AMI-7001) were chosen with the same polymer backbone based on polystyrene polymer crosslinked with divinyl benzene for better comparison. However, CMI-7000 has sulfonic functional group in sodium ion form and AMI-7001 has quaternary ammonium functional group in chlorine ion form as shown in Fig. 1. Therefore, the CMI-7000 membrane was treated with H_2SO_4 to exchange the sodium ions by hydrogen ions in order to get the membrane in proton form. Similarly, AMI-7001 in hydroxyl form was prepared by treating with KOH as shown in Fig. 1.

3.2.2. Membrane electrode assembly

Pt/C (40 wt% Pt) and nafion dispersion was used to prepare the anode catalyst ink. The prepared catalyst ink was coated onto a carbon paper using spraying technique and dried to obtain the anode electrode. The Pt/C catalyst loading was kept at 0.5 mg cm^{-2} at the anode. The cathode was developed by electroplating of copper onto the carbon paper. Electrodeposited copper on the carbon paper was then thermally treated to obtain cuprous oxide. The Cu_2O/C with 2 mg cm^{-2} was used as cathode in dERC reactor for further study. The membrane electrode assembly was prepared by sandwiching the SPE in between anode and cathode electrodes at around 50 kg cm^{-2} and 90 °C.