Applied Catalysis B: Environmental 181 (2016) 88–93

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Simultaneous electrocatalytic reduction of dinitrogen and carbon dioxide on conducting polymer electrodes

Didem Balun Kayan*, Fatih Köleli

Department of Chemistry, Science and Arts Faculty, Mersin University, 33342, Mersin, TURKEY

ARTICLE INFO

Article history:
Received 28 May 2015
Received in revised form 15 July 2015
Accepted 24 July 2015
Available online 29 July 2015

Keywords:
N_2-Reduction
CO_2-Reduction
Conducting polymer
Urea formation

ABSTRACT

The conversion of carbon dioxide with nitrogen containing compounds into valuable materials consistings of C—N bond is a very attractive research area due to today's energy requirements. The simultaneous electrocatalytic reduction of carbon dioxide and dinitrogen was investigated at 60 bar (30 bar N_2 + 30 bar CO_2) in this study. The electrochemical reduction was achieved on polyaniline (PAni) and polypyrrole (PPy) coated platinum electrodes at −0.165 V, the lowest possible overpotentials, known in the literature. The main products from the CO_2 and N_2 reduction were ammonia, urea and formic acid. The electrochemical reduction performed in an aqueous 0.1 M Li_2SO_4/0.03 M H^+ solution was characterized by using cyclic voltammetry, potentiostatic electrolysis and Tafel diagrams in order to analyze the polymer selectivity as well as its reactivity as a function of the applied potential. Hence, CO_2 and N_2 were converted into value added chemicals, which included urea; an important raw material for the chemical industry with high nitrogen content.

1. Introduction

The reduction of dinitrogen to ammonia is a natural process, which is conducted by certain micro-organisms using a nitrogenase enzyme. When this essential chemical process occurs in nature it is based -like almost all natural processes- on a sensitive dynamic equilibrium. However, this process is too slow for use at a technical scale and a large amount of energy is needed for the reduction due to the strong triple bond in the N_2 molecule [1–4].

Many attempts have failed to reduce N_2 to amine on bulk metal catalysts due to the fast hydrogen evolution and chemical inactivity of N_2 [5,6]. In addition, based on the operating principles of chlorophyll, some organometallic compounds have been employed to reduce N_2 [7–10].

Due to the similarity to photosynthesis, researchers were stimulated to convert CO_2 under laboratory conditions into organic compounds. Different methods were proposed for CO_2 reduction with homogeneous and heterogeneous systems [11–17]. Among these methods, electrochemical reduction appears to be the most appropriate one, which is why the electro-reduction of CO_2 to valuable products became the aim of many studies with substantial interest in the recent time [18]. This interest was inspired, firstly, by the need to prevent the greenhouse effect, in which CO_2 plays a primarily role, and secondly, by it being an economic C-source available in huge amounts in the atmosphere.

Employing bulk metal catalysts for CO_2 reduction leads to different substances depending on the metal used as the electrode and on the electrolyte [19]. In an aqueous acidic medium, the main substances are HCOOH and CO. Nevertheless, the application of an aprotic medium leads mostly to hydrocarbons. Although the handling of bulk materials is easy, bulk metal electrodes have the disadvantages of a reduction that occurs at relatively high negative overpotentials. In the literature, the best results were obtained between −1.8 to −1.9 V. However, these high overpotential values could be decreased to ca. −0.4 V by the application of conducting polymers, deposited on the metal surface, in aprotic as well as in aqueous media [14,20].

Urea is commercially produced by the reaction of ammonia and carbon dioxide at a high pressure (100–200 atm) and temperature (about 180 °C). The reaction product, ammonium carbamate, dehydrates rapidly to urea and water. Due to the high energy requirement of these thermic processes, new methods are needed that can convert carbon dioxide, dinitrogen and hydrogen to nitrogen containing substances under mild conditions [21]. It should be emphasized that in contrast to the H^+ and CO_2 reduction, only a few electrocatalysts have been reported to exhibit any activity for N_2 reduction. There are also very few studies on the simultaneous

---

* Corresponding author. Present address: Department of Chemistry, Science and Arts Faculty, Aksaray University, 68100, Aksaray, Turkey. Fax: +90 382 288 21 25.
E-mail address: didembalun@aksaray.edu.tr (D.B. Kayan).

http://dx.doi.org/10.1016/j.apcatb.2015.07.045
0926-3373/© 2015 Published by Elsevier B.V.

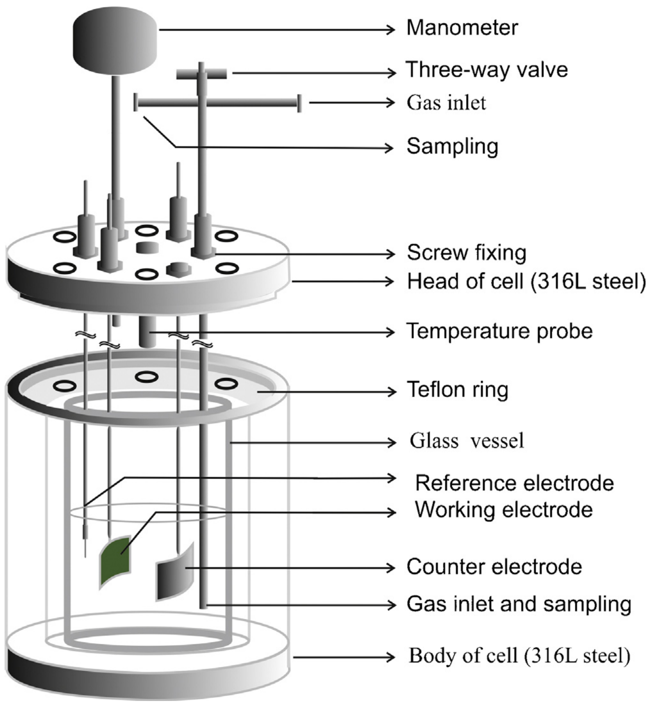

Fig. 1. High pressure cell.

reduction of carbon dioxide and nitrogen containing materials in the literature [22–26].

The electrochemical reductions of N_2 and CO_2 were investigated separately in aqueous medium in our previous studies [27–29], and we could reduce these substances with the application of the lowest possible overpotential values (–0,4 V NHE) – from the literature – to valuable substances. Now, we present the results of a simultaneous, one step reduction of both N_2 and CO_2 gases, in the same ambiance to the obtain urea with the lowest possible energy input (overpotential) on polyaniline and polypyrrole coated platinum electro-catalysts, for the first time.

2. Experimental

Polyaniline and Polypyrrole films were deposited on a Pt plate (8 cm^2) by cyclic voltammetry technique. Polymerization of aniline was achieved from solution containing 0.1 M aniline in 0.5 M H_2SO_4. At the first polarization cycle the potential swept between –0.20 V and +1.20 V [Ag/AgCl], the other following cycles swept continuously between –0.20 and +0.85 V to protect the film from overoxidation. Scan rate was 0.05 V/s throughout the measurements. Electro-polymerization was performed in a three electrode H-type cell using a platinum plate (8 cm^2) as a counter electrode. After polymerization, the coated electrodes were dipped into methanol for a few minutes to take away surplus ions, washed carefully with water and then transferred into the electrochemical high-pressure cell (Fig. 1). Film thicknesses were determined using the charge value of the first anodic peak of the last growth cycle during PAni film formation. The optimum film thickness of the PAni was calculated as 1.52 μm after 35 cycles.

The polypyrrole films were also grown potentiodynamically from solution containing 0.1 M pyrrole/0.5 M $LiClO_4$/acetonitrile by cycling the potential from 0.00 V to +1.45 V for the first cycle and 0.00 V to +0.90 V for the following cycles at a scan rate of 0.05 V/s. The thicknesses of the PPy layer were calculated by coulometric oxidation technique as 0.73 μm after 5 cycles.

The coated samples were rinsed thoroughly first with methanol and then water for removing the residual reactants from the polymer films.

The simultaneous reduction of dinitrogen and carbon dioxide was achieved in an electrochemical high-pressure cell where the coated polymer electrodes were used as working electrodes. The counter electrode was a Pt plate (8 cm^2) and a $Pb(Hg)_x/PbSO_4/SO_4{}^{2-}$ was used as a reference electrode with reference potential −0.1 V[NHE]. An Electrochemical Workstation (CHI 660B) was employed for voltammetric measurements between −0.1 V and −0.325 V [NHE]. The preparative electrolysis time was determined experimentally as 5 h. The amounts of ammonia and/or urea produced in the electrolyte were established by the spectrophotometric indophenol method [30].

The reduction product of CO_2 was only formic acid (formate) and it was analysed by HPLC [Agilent 1200; ODS-H-OL column; UV/Vis detector (210 nm); carrier phase: H_2SO_4 solution pH 4; flow rate 2 ml/min]. After electrolyses, a gas sample (1.0 ml) was taken and analyzed by GC (HP 6810; Porapak-QS; FID; 50 °C; He as carrier gas) for possible production of gaseous products.

All reactions were carried out in aqueous 0.1 M Li_2SO_4/0.03 M H^+, under total pressure of 60 bar including 30 bar N_2 and 30 bar CO_2.

3. Results and discussion

The simultaneous electrochemical reduction of dinitrogen and carbon dioxide was investigated on polymer coated Pt-plate electrodes using both cyclic voltammetry and constant potential electrolysis techniques. Polyaniline and polypyrrole were used to modify the bulk metal surface. These two polymeric materials showed different behaviours in current density and product yields. Control experiments were done on the blank Pt electrode at all applied potential range under 30 bar N_2 and 30 bar CO_2 atmosphere in order to ensure the activity of the deposited conducting polymers and also under 60 bar Ar on the PAni and PPy coated Pt electrode under same conditions. There was no product formation in both cases.

3.1. Voltammetric investigations

The cyclic voltammograms (CV) of the PAni-coated and PPy-coated Pt electrodes are presented in Fig. 2.

Fig. 2 shows the CVs of the PAni and PPy coated Pt plate electrodes (8 cm^2) under a total pressure of 60 bar (30 bar N_2 + 30 bar CO_2) in 0.1 M Li_2SO_4/0.03 M H^+. These CVs show the main features of the electro-reduction of the proton to form an atomic hydrogen (H_{ad}). In other words, the electrode process comprises an electron transfer step followed by the possibly of a slow chemical step via Reactions 1–3 as shown below.

$$H^+ + e^- \rightarrow H_{ad} \qquad (1)$$

$$N_2 + H_{ad} \rightarrow N_2H_{ad} \qquad (2)$$

$$N_2H_{ad} + 5H_{ad} \rightarrow 2NH_3 \qquad (3)$$

During the measurements/preparative electrolyses, the reduction current was noticeably higher at the PPy coated electrode than the PAni; this result was also verified by the product formation. Therefore, we could determine the higher product concentrations on the PPy modified catalysts.

3.2. Electro-reduction on PAni coated Pt electrode

The reaction products of the simultaneous electrochemical reduction of dinitrogen and carbon dioxide were ammonia, urea