



Electrochemical reduction from carbon dioxide to urea through the application of a polycrystalline palladium electrode potential Square Wave Regime

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The electrochemical reduction of CO₂ saturated in a 0.1 M NH₃ solution for 4 h is very efficient into useful organic production. The substance resulting from electrochemical of CO₂ reduction in palladium electrode was urea (CO(NH₂)₂) by application square wave potential, with optimized faradic efficiencies (FE) of 36.8 and 17.7%. In this proof-of-concept electrochemical CO₂ reduction study, mechanistic details of the reaction paths are identified and suggested in the CO₂ capture medium. The square wave potential rang lower and upper between -1.0 and 0.4 V with a 100 Hz frequency. Cyclic Voltammetry, UV-Vis spectrometry, Infrared spectroscopy, NMR, MASS spectra, TLC plate and TGA thermogravimetry were used to characterize the electrochemical system, analyzed and products formed. The results obtained from these techniques provided sufficient evidence that the product upon application of a square wave potential regime to a palladium electrode in a CO₂-saturated NH₃ solution was urea. The conversion rate of CO₂ reduction to urea is 3.85×10⁻⁵ mol/L.h.cm².

Keywords: Square wave, potential regimes, electrochemical reduction, CO₂ reduction, palladium electrode, urea production.

Introduction

The potential carbon resource on earth is carbon dioxide. Over the last two decades, it has also been a greenhouse gas with a rising atmospheric concentration. Chemical CO₂ fixing is an attractive technique for using carbon resources and reducing the atmospheric CO₂ concentration. Nevertheless, CO₂ is the stablest among carbon-based substances under the environmental conditions. It has not been incorporated as a major industrial material¹. Once captured, CO₂ is a potentially useful feedstock if it can be converted into formate/formic acid, carbon monoxide, or more highly reduced hydrocarbon products^{2,3}. Many researchers, however, advocate that the best strategy for reducing carbon dioxide in the atmosphere be by reusing carbon dioxide as a carbon-natural raw material and feedstock for industrial processes⁴. That is an imitation of our Mother Nature photosynthesis and solving the problem of increasing concentration of carbon dioxide by rendering the excess carbon dioxide part of the cycle of carbon in nature⁵. Many approaches have been adopted for reduction of carbon dioxide. These approaches include thermochemical, photochemical, electrochemical, biochemical, photochemical, photoelectrochemical,

bioelectrochemical, photoelectrochemical and electrochemical⁶. The electrochemical approach for reduction of CO₂ received great attention because the reduction process can be carried out at ambient conditions⁷. The electrochemical of carbon dioxide is an important technology option for decrease percent of carbon in the atmosphere and conversion CO₂ to other organic materials, because the electrochemical reduction of CO₂ have high efficiency and high reaction rates for conversion CO₂⁸⁻¹⁰. The carbon dioxide electrochemical reduction was found to show great dependence on the material of the electrode, the solvent and the supporting electrolyte¹¹. The literature surveyed, however, did not show emphasis on the applied potential regime in addition to the used electrocatalyst, the solvent and the supporting electrolyte. In this context, the square wave potential regime is a train of pulses between two potential limits, which approximates in electrochemical terminology a repetitive double potential step waveform¹². In each pulse one or more of electrochemical events occur and, their inverse, though not necessarily, occur upon reversal¹³. Some intermediates might be created and their fate is affected by the square wave parameters¹⁴. Some of transition metal electrodes have been used to elec-

trochemical reduction of CO₂ to carbon monoxide (CO)^{15–17}. Square wave potential one of electrochemical methods used for different applications (prepared nanoparticle, oxide layers and reduction of CO₂). The one of advantage square wave is minimizes most of the undesired effects, the square wave voltammetry is related to signals which corresponds to the current reaction. CO is formed more with low potential than with high potential by applying square wave potential in electrical chemistry^{18,19}. In this study, the electrochemical reduction of CO₂-saturated in 0.1 M NH₃ to useful organic product by using a square wave potential regime at palladium electrode, namely urea. The novelty of the present work emanates from the combination of using a suitable electrocatalyst and the appropriate applied potential regime, in this case, the square wave potential regime. This proves the notion that electrocatalysis can be brought about by marrying between the good choice of the electrocatalyst and the appropriate potential regime.

Experimental

Instruments and materials:

Potentiostat (273A Princeton Applied Research-Echem software) was used for control of the experiment and data acquisition. Function generator (Bk Precision, 4003A). FTIR spectrophotometer (Thermo Nicolet Nexus-670). ¹H, ¹³C and DEPT-NMR spectra (Bruker Avance III 500 MHz spectrometer). UV-Vis spectrophotometer (Varian Cary 100). High-resolution mass spectra HRMS (a Bruker APEX-IV instrument). Thermogravimetric TGA (Netzsch thermal analyzer-Model STA 409 PC/PC).

A two-compartment electrochemical cell was used for voltammetric measurements and electrochemical reduction of CO₂. Three-electrode configuration working electrode was a 1 cm² palladium foil, spot welded to the end of a palladium wire (99.95%, Sigma-Aldrich), the auxiliary electrode was made of about 3 cm² platinum gauze (Aldrich, 99.99%) spot welded to the end of a platinum wire and the reference electrode was an Ag/AgCl/[Cl⁻] is 1.0 M, and all the reported potentials are referenced to this electrode. The supporting electrolyte were sulfuric acid (Merck, Germany) and ammonia solution 25% (LABCHEM, USA). All solutions dissolved in Milli-Q water (Millipore, Merck). The International Company for Industrial and Medical Gases supplied N₂ and CO₂

gases (G5 grade, 99.999% purity).

The palladium foil electrode was used for generation of organic species by reduction of carbon dioxide, while the palladium wire electrode was used as voltammetric sensors for detection of any change to the chemistry of the solution.

Procedures:

The cell was cleaned and washed with Milli-Q water thoroughly. The electrochemical cell solution is purged in the solution of O₂ gas with N₂ gas for 10 min. Scanning potential voltammograms of palladium electrodes (in the region –0.2 to 1.2 V at 100 MV/s for about 15 cycles in 0.5 M H₂SO₄) to obtain baseline current response. The electrolyte solution is purged with CO₂ gas around 20 min to saturate the solution before application square wave potential region at pure palladium electrodes between 0.4 V to –1.4 V for 4 h. After applying, a square wave in the cell was analyzed CO₂ reduction product.

The changes observed on the voltammograms are dependent on the concentration of the impurities in the solution or the impurities coverage on the surface of the electrode. For this, reproducing the well-known cyclic voltammograms of the polycrystalline palladium electrode in H₂SO₄ was taken as a criterion for a verified-clean electrochemical system including the electrode, the supporting electrolyte and the purging gas.

A function generator was developed to supply the square wave with the predefined frequency and amplitude. The desired amplitude, upper and lower potential limits of the square wave were controlled jointly by the potentiostat and the function generator. All experiments were performed at ambient conditions.

Results and discussion

The cyclic voltammetry at palladium electrode:

Cyclic voltammetry of the palladium electrode in 0.5 M H₂SO₄ is shown in Fig. 1. The CV was recorded over a wide potential range between –0.2 to +1.20 V at a scan rate $v = 100 \text{ mV s}^{-1}$, CV scans recorded after applying a square wave potential regime to CO₂-saturated in 0.1 M NH₃ solution for four hours. Shows in Fig. 1 the cyclic voltammogram indicates some differences between two scans after adding 5 ml of organic product by the square wave potential of a palla-

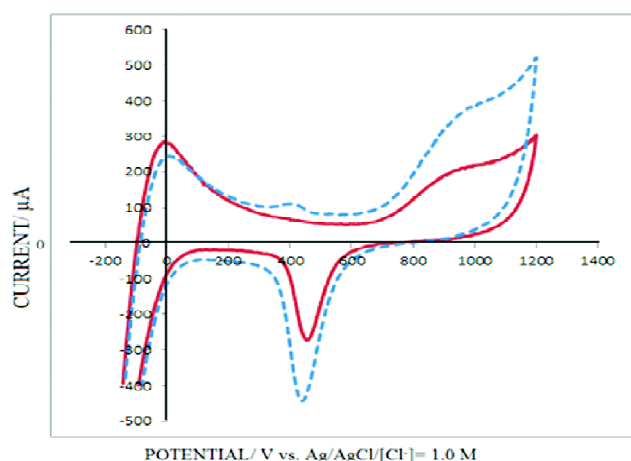


Fig. 1. The cyclic voltammograms of a polycrystalline palladium electrode in 0.5 M H₂SO₄ (—) and in (.....) 0.5 M H₂SO₄ to which 5 ml of the square wave treated solution is added. $dE/dt = 100$ mV/s.

dium electrode. The change of the hydrogen absorbed region depends strongly on the electrode potential with organic in solution, the potential region of oxidation can be distinguished on the two voltammograms by a small peak current occurred at 0.4 V and the height of oxygen adsorption/desorption region obtained from the oxidation charges also be observed in CVs for Pd electrode.

Moreover, the CV experiments using a palladium electrode immersed in a 0.5 M H₂SO₄ with 5 ml of solution after applying a square wave clearly show that existence some certain species in solution. This behavior reflects the fact that in an electroreduction experiment CO₂ convert by applying a square wave potential in 0.1 M NH₃ solution to organic production. The CVs scan was observed increase peak current at 0.4 V can be related to the square root of scan rate (peak current $\propto v^{1/2}$, $n^{1/2} = 5, 7.5$ and 10 mV s⁻¹) of palladium electrode. These evidences of the electroreduction of CO₂ occur from the bulk solution in the cell²⁰.

UV-Vis spectrophotometry:

UV-Vis spectroscopy is one of the most valuable tests for proof organic species' existence in solution. The UV-Vis spectra resulting from product electroreduction of CO₂ saturated in 0.1 M NH₃ solution by applied square wave potential for Pd electrode. The wavelength was scanned in the range of 200–400 nm to determine the absorbance peak of product electrochemical reduction of CO₂. From the UV spectrum of

organic product, absorption maxima was found to be 204 nm (λ_{max}). The peak in UV-Vis spectra is too intense to obtain reliable absorbencies of organic produce in solution.

The absorption band p-p* in UV spectrums changed over of urea to a longer wavelength. Because of the hydrogen bond between C=O...N-H of urea, the bond length of C=O is increased and the energy needed for the transition is therefore smaller, and the absorption shows the red spectrum end²¹.

Mass spectrometry (LC-MS):

The analysed of the organic product by LC-MS to determine molar weight and fragmentation of compound after applied square wave potential regime at palladium electrode immersed in a CO₂-saturated NH₃ solution in Fig. 2. The fragmentation of organic product (urea) was observed on the mass fragmentation spectrum in Fig. 2. Here, the major ions observed in the positive ESI-MS mode spectrum, the urea fragments were at m/z 59.2, 43.1 and 31.0. The most intense fragment at m/z 59.2 is assumed to be the peak of the parent ion CO(NH₂)₂, the ion at m/z 43.1 was formed upon loss of an NH₂ to form CO(NH₂)⁺ and ion at m/z 31.0 for loss of the NH₂ atoms leads to the formation of CO. The m/z 40.9 was considered as argon in the ambience. The m/z 43.9 was attributed to carbon dioxide evolved during decomposition of urea. Some other peaks in the spectrum are attributed to the supporting electrolyte. This increases our confidence that the mass spectrometry is optimized for the fragmentation behavior of the urea upon application of a square wave potential regime²².

IR spectrometric measurements:

The organic product our investigation of infrared absorption spectra in Fig. 3, it was necessary to examine the absorption spectrum of urea product. The urea product of reduction CO₂ saturated in 0.1 M NH₃ solution by applied square wave potential for polycrystalline Pd electrode. Show in IR absorption spectrum of urea: two bands: the N-H stretching vibrations form 3424.69 and 3327.44 cm⁻¹. 2354.57 cm⁻¹ this band to bending NH₂ motions. An absorption band observed at 1677.61 cm⁻¹ corresponds to NH₂ rocking vibrations. Assigned this band to C=O stretching vibrations at 1586.85 cm⁻¹. The frequency 1454.91 cm⁻¹ should be assigned to C-N stretching vibrations in agreement with re-

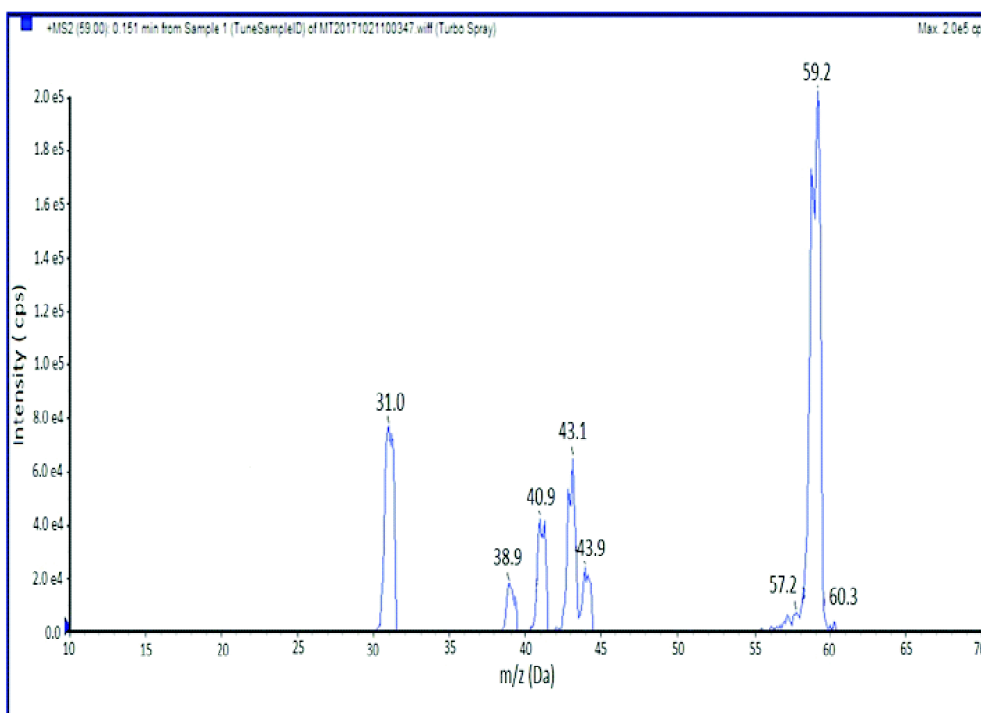


Fig. 2. The mass spectrum of the solid residue of the solution after application of a square wave potential regime to a palladium electrode in a CO₂-saturated NH₃ solution.

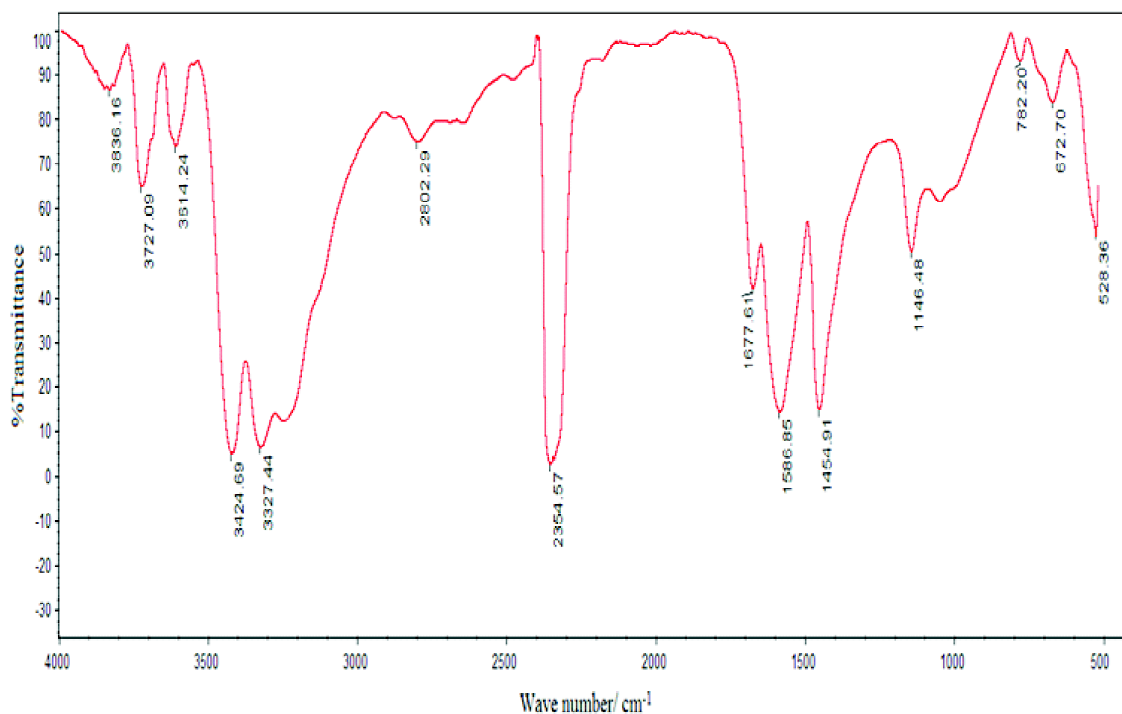


Fig. 3. IR spectrum for the solid residue of CO₂ saturated NH₃ solution after application of a square wave potential regime to a palladium electrode in the above-mentioned solution.

sults of former investigators, assigned it 1146.48 cm^{-1} to C symmetric. Thus, the infrared data supports the conclusion that the melting point of urea is 133°C ²³. Since the compound contains conjugated C=O bond as indicated by UV-Vis data, and the compound is expected to be a low molecular weight compound. However, organic product by electrochemical reduction of CO_2 was examined in the solids collected. This spectrum is very typical for a urea inclusion solution^{23,24}.

NMR results:

The electroreduction of carbon dioxide at palladium electrode to urea was analyzed by ^1H , ^{13}C and DEPT-NMR spectra are shown in Fig. 4. In the ^1H NMR spectrum, the chemical shift of proton (H) signal is observed a single peak at 4.64 ppm in Fig. 4(a). The ^{13}C NMR of organic product give

signals to one peak at 162.77 ppm, the spectrum in Fig. 4(b) shows only one type of carbon atom in compound for C=O (carbonyl) group in urea in D_2O solvent. The DEPT-135 scan in the range of 0–180 ppm, but the spectrum have not any peak, which indicates the absence of CH, CH_2 or CH_3 groups in Fig. 4(c). Their NMR spectra was obtained by analysis good agreement with urea molecule²⁵.

Thermogravimetric analysis (TGA):

TGA and DTG were used to study the decomposition of organic product (10 mg urea sample of the dry sample) after applying a square wave from the CO_2 -saturated 0.1 M NH_3 for palladium electrode in Fig. 5. TGA shows the analyzed the heating rate influence on organic product (urea), hence the greater mass loss with increased heating. The sample was heated between 50°C to 500°C in an alumina crucible at

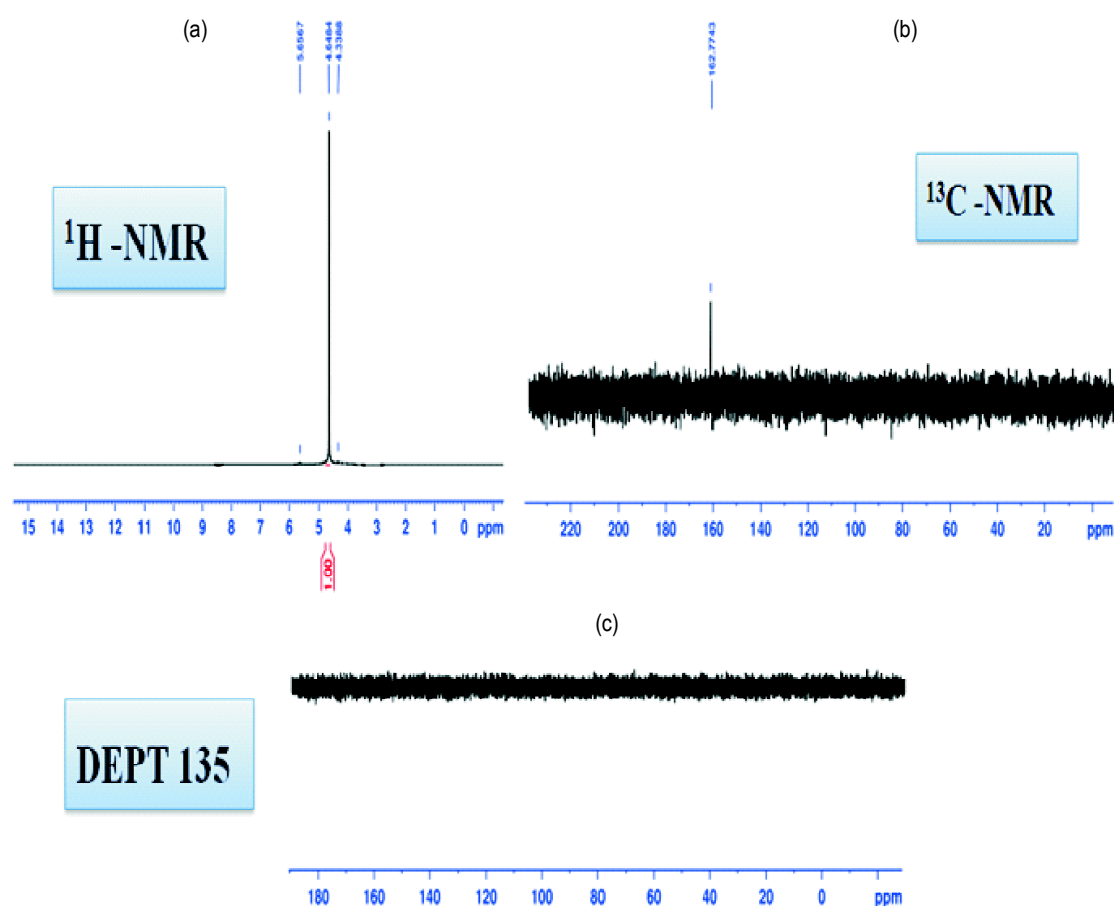


Fig. 4. NMR spectra for the solid residue of CO_2 -saturated NH_3 solution after application of a square wave potential regime to a palladium electrode in the above-mentioned solution: (a) ^1H NMR, (b) ^{13}C NMR and (c) DEPT-135.

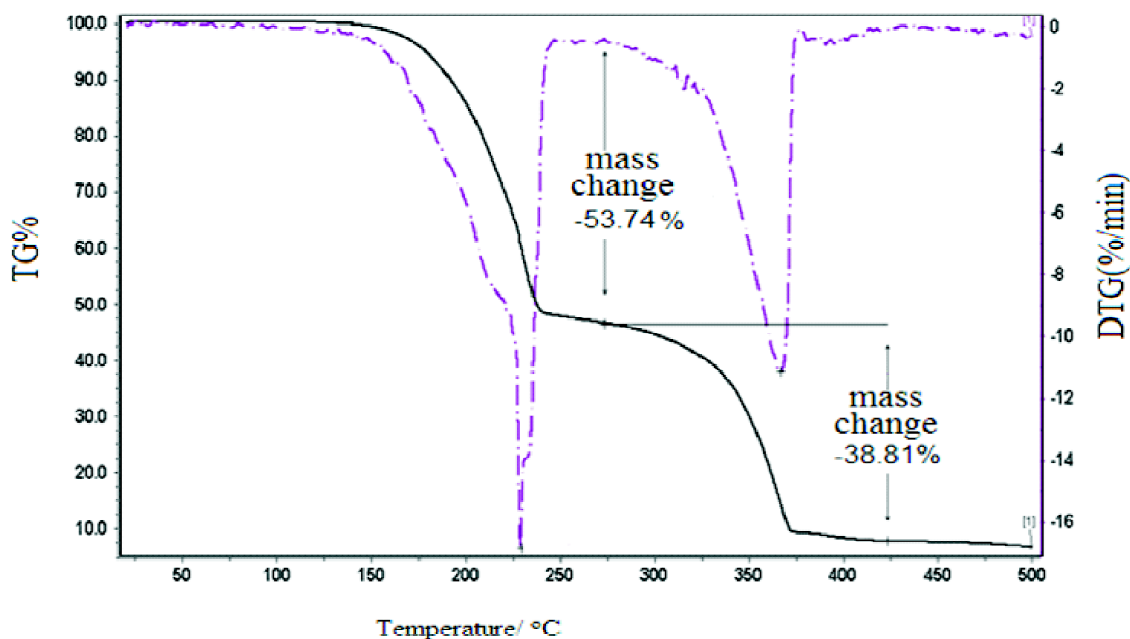


Fig. 5. TGA and DTG thermograms for the solid residue of the solution after application of a square wave potential regime to a palladium electrode in a CO_2 -saturated 0.1 M NH_3 solution.

a heating rate of $10^\circ\text{C}/\text{min}$ using N_2 as purge gas. Show in Fig. 6 two major stages of mass loss of urea. The found that when it was heated at 200 to 250°C the loss in weight is 53.74% and an additional weight loss of 38.81% in the range of 300 to 450°C was observed²¹. Finally, the residual mass of the sample was degraded approximately 7.94% at 500°C . The TGA experiments proved that the organic product is urea²².

Thin layer chromatography (TLC):

TLC plates made with silica have been used in the separation of organic product (urea) after applying a square wave for Pd electrode. The first air was dried at room temperature and heated at 100°C for 1 h. The three points of organic product (urea) and urea standard were injection onto approximately 2 cm above the lower edge of the TLC plate by a micropipette. The mobile phase solvent is (1-butanol 80 ml, acetic acid 20 ml and water Milli-Q 20 ml). The similar yellow spot between urea sample and standard this prove the organic product of electrochemical reduction of CO_2 is urea. TLC plate bands passed over the urea area and contained urea. The separation of urea was also varied from 20 to 30%, the spot loading was $5\ \mu\text{g}$ of each compound. In the pres-

ence of urea, both components appeared in a diffuse spot at R_f 0.46–0.61.

Rate of CO_2 reduction:

Experimentally determined concentration of organic production and the rate of conversion of CO_2 in NH_3 to urea by spectrophotometrically (UV-Vis) at maximum absorption values is 204 nm. The absorption spectra of organic product (urea) and urea standard were measured after applying the square wave potential of Pd electrodes for 4.0 h. The Table 1 shows the concentration and absorbance peak of product electrochemical reduction CO_2 and urea standard according to Fig. 6. In order to determine the conversion rate, firstly, one has to determine the concentration of urea. These were peaks of concentration urea in UV-Vis. As can be seen, the absorption peak of urea sample similar to absorbance of urea standard at $1 \times 10^{-4}\ \text{M}$ in Fig. 6. Accordingly, the concentration of urea was $1.08 \times 10^{-3}\ \text{M}$. The conversion rate is counted by use of eq. = $[(\text{Conc}_{\text{sample}} - \text{Conc}_{\text{standard}})/\text{time}]/\text{area of surface electrode}$, the average rate of conversion was $3.85 \times 10^{-5}\ \text{mol/L.h.cm}^2$ ²⁶. The yield of urea depends on several factors including the catalyst, the reaction temperature and the reaction time²⁸.

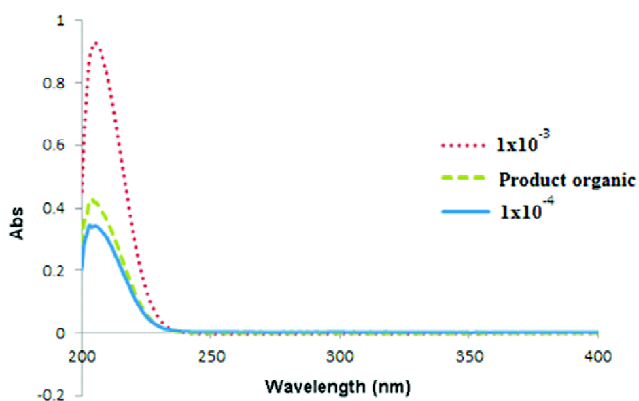


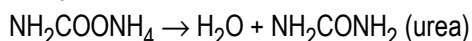
Fig. 6. UV-Vis spectrum of the CO₂ saturated 0.1 M NH₃ solutions after application of the square wave regime using Pd electrode with urea standard.

Table 1. Concentration and absorbance of the urea sample and standard by UV-Vis after applying a square wave regime of CO₂-saturated 0.1 M NH₃ at Pd electrode

Concentration (M)	Abs
1×10 ⁻³ M (urea standard)	0.9
Produces organic (urea)	0.41
1×10 ⁻⁴ M (urea standard)	0.38

The CO₂ electroreduction mechanism:

The electrochemical reduction of CO₂-saturated in NH₃ solutions. The major products are (H₂NCONH₂). Urea consists of carbon dioxide and ammonia in a two-step reaction the urea forms. The area contains unreacted NH₃ reaction with CO₂ radical anion with the solution give ammonium carbamate (NH₂COONH₄) in step two NH₂COONH₄ decomposes to NH₂CONH₂ (urea) and H₂O. Urea is produced from CO₂ and NH₃ in two equilibrium reactions, the suggested mechanism is described in the following scheme²⁷:



The carbon dioxide could first be captured by ammonia in an organic solvent, to obtain ammonium carbamate, before the solid product is used to produce urea. In the second step of the process, the pure ammonium carbamate is used to produce urea with good yield (up to 54% on carbamate basis) at 393–413 K in the presence of inexpensive catalysts. The process involves the intermediate formation of ammonium carbamate that is successively dehydrated to form urea²⁸.

Conclusions

In this study, the electrochemical reduction of CO₂ by applying a square wave potential at the palladium electrode in 0.1 M NH₃ electrolyte has been investigated. Electrochemical reduction from carbon dioxide to urea (NH₂CONH₂) is interesting. Many of the instruments (UV-Vis spectroscopy, NMR, LC-MS, IR, TLC, thermogravimetry and cyclic voltammetry techniques) investigated the urea product by electrochemical reduction of CO₂. The rate of conversion of CO₂ to urea was far from complete conversion due to the low solubility of CO₂ in aqueous solutions at ambient conditions but still indicative of the possibility of conversion. The conversion rate of urea was 3.85×10⁻⁵ mol/L.h.cm². Improvement of the rate of conversion through a judicious design of a new pressurized continuous flow dynamic electrochemical cell have been studied.

References

1. S. G. Pritchard, *Plant Pathology*, 2011, **60**(1), 82. doi: 10.1111/j.1365-3059.2010.02405.x.
2. G. Lu, H. Wang, Z. Bian and X. Liu, *The Scientific World Journal*, 2013, 1. doi: 10.1155/2013/424617.
3. Y. Hori, *Modern Aspects of Electrochemistry*, 2008, 89. doi: 10.1007/978-0-387-49489-0_3.
4. A. Skorek-Osikowska, J. Kotowicz and K. Janusz-Szymańska, *Energy & Fuels*, 2012, **26**(11), 6509. doi: 10.1021/ef201687d.
5. B. Sørensen, *Renewable Energy Conversion, Transmission and Storage*, 2007, 127. doi: 10.1016/b978-012374262-9.50017-3.
6. R. Kas, K. Yang, D. Bohra, R. Kortlever, T. Burdyny and W. A. Smith, 2019, doi: 10.26434/chemrxiv.10032278
7. J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**(2), 631. doi: 10.1039/c3cs60323g.
8. H. Hashiba, S. Yotsuhashi, M. Deguchi and Y. Yamada, *ACS Combinatorial Science*, 2016, **18**(4), 203. doi: 10.1021/acscombsci.6b00021.
9. D. R. Kauffman, J. Thakkar, R. Siva, C. Matranga, P. R. Ohodnicki, C. Zeng and R. Jin, *ACS Applied Materials & Interfaces*, 2015, **7**(28), 15626. doi: 10.1021/acsami.5b04393.
10. M. Gattrell, N. Gupta and A. Co, *Energy Conversion and Management*, 2007, **48**(4), 1255. doi: 10.1016/j.enconman.2006.09.019.
11. T. Zaki, "Application of Metal Organic Frameworks in Carbon Dioxide Conversion to Methanol. Conversion of Carbon Dioxide into Hydrocarbons", Vol. 2, Technology Environmental Chemistry for a Sustainable World, 2019, 75. doi: 10.1007/978-3-030-28638-5_3.
12. E. R. Martínez and J. M. S. Hervás, *Catalysis*, 2020, **1**, 165. doi: 10.1007/978-3-030-28622-4_7.

13. Y. Chen, C. W. Li and M. W. Kanan, *J. Am. Chem. Soc.*, 2012, **134**(49), 19969. doi: 10.1021/ja309317u
14. H. A. Hansen, J. B. Varley, A. A. Peterson and J. K. Nørskov, *J. Phys. Chem. Lett.*, 2013, **4**(3), 388. doi: 10.1021/jz3021155.
15. H. Hashiba, S. Yotsuhashi, M. Deguchi and Y. Yamada, *ACS Combinatorial Science*, 2016, **18**(4), 203. doi: 10.1021/acscmbosci.6b00021.
16. K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy and Environmental Science*, 2012, **5**(5), 7050. doi: 10.1039/c2ee21234j.
17. K. P. Kuhl, T. Hatsukade, E. R. Cave, D. N. Abram, J. Kibsgaard and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2014, **136**(40), 14107. doi: 10.1021/ja505791r.
18. M. Dunwell, Q. Lu, J. M. Heyes, J. Rosen, J. G. Chen, Y. Yan, and B. Xu, *J. Am. Chem. Soc.*, 2017, **139**(10), 3774. doi: 10.1021/jacs.6b13287.
19. J. González, A. Molina, N. Abenza, C. Serna and M. M. Moreno, *Anal. Chem.*, 2007, **79**(19), 7580. doi: 10.1021/ac071006a.
20. A. S. Varela, C. Schlaup, Z. P. Jovanov, P. Malacrida, S. Horch, I. E. L. Stephens and I. Chorkendorff, *J. Phys. Chem. C*, 2013, **117**(40), 20500. doi: 10.1021/jp406913f.
21. G. Madhurambal, M. Mariappan and S. C. Mojumdar, *Journal of Thermal Analysis and Calorimetry*, 2010, **100**(3), 763. doi:10.1007/s10973-010-0758-0.
22. J. P. Chen and K. Isa, *Journal of the Mass Spectrometry Society of Japan*, 1998, **46**(4), 299. doi:10.5702/massspec.46.299.
23. S. Samaržija-Jovanović, V. Jovanović, S. Konstantinović, G. Marković and M. Marinović-Cincović, *Journal of Thermal Analysis and Calorimetry*, **104**(3), 1159. doi: 10.1007/s10973-010-1143-8.
24. V. Jovanović, S. Samaržija-Jovanović, B. Dekić, V. Dekić, M. Marinović-Cincović, G. Marković and S. Konstantinović, *Journal of Thermoplastic Composite Materials*, 2012, **27**(5), 632. doi: 10.1177/0892705712453156.
25. E. E. Ferg, A. Pizzi and D. C. Levendis, *J. Appl. Polym. Sci.*, 1993, **50**(5), 907. doi:10.1002/app.1993.070500519.
26. G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1954, **26**(3), 452. doi: 10.1021/ac60087a006.
27. X. Xiang, L. Guo, X. Wu, X. Ma and Y. Xia, *Environ. Chem. Lett.*, 2012, **10**(3), 295. doi: 10.1007/s10311-012-0366-2.
28. F. Barzagli, F. Mani and M. Peruzzini, *Green Chem.*, 2011, **13**(5), 1267.