

Doctoral (Ph.D.) Theses

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**ELECTROCHEMICAL REDUCTION OF CARBON
DIOXIDE ON NITROGEN-DOPED CARBON
ELECTRODES**

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1. Introduction and aims

A grand challenge of today's society is the transition from the fossil fuel-based energy production and chemical industry to the use of renewable energy to maintain a sustainable energy supply. Electrochemical reduction of CO₂ to fuels and commodity chemicals is very attractive in this regard. On one hand, it utilizes a greenhouse gas as a starting material, of which atmospheric concentration has increased significantly in recent years. On the other hand, the energy demand of the process can be easily supplied by renewable energy sources (e.g., solar or wind), of which price has dropped greatly in recent years. Therefore, we could store the intermittent renewable energy in the form of chemical bonds, while alleviating environmental impacts caused by excess atmospheric CO₂. Electrochemical reduction of CO₂, however, will only be competitive to the existing technologies if more efficient electrocatalysts are developed.

The (metal)-nitrogen-doped carbon materials are very promising new-generation catalysts in the CO₂ reduction reaction. They have many advantages compared to the most efficient (precious) metal catalysts:

- They can be synthesized by relatively simple and cheap methods;
- Several properties can be tuned during the synthesis process;
- The presence of nitrogen atoms in the carbon structure is favorable for the adsorption and activation of CO₂;
- They generally possess good electric conductivity;
- High surface areas can be reached as a result of the porous structure;
- They have good mechanical, chemical and thermal stability.

Although significant improvement has been achieved in the last decade in the field of M–N–C catalysts, there are still many open questions regarding the factors determining their CO₂ reduction performance.

The investigation and development of CO₂ reduction catalysts is one of the main research topics in the Photoelectrochemistry Research Group at the University of Szeged. As a new research direction in the beginning of my doctoral studies we started to study the electrocatalytic properties of **N-doped carbon electrodes**. **Our aim was to shed light on the main factors dictating the CO₂ reduction performance of these new generation catalysts by studying the reduction mechanism and the effect of different materials properties on the reduction activity.**

Our first goal was to find out **what is the actual reacting species in the CO₂ reduction at the surface of the N–C catalysts**. For this purpose, we carried out selective isotopic labeling studies in combination with pH-dependent electrolysis experiments. Then, we focused on the physical-chemical properties of the N–C materials. We aimed to synthesize catalysts, which were closely identical in their physical-chemical properties and only differed in their porosity. Therefore, we could use this set of catalysts as a model system to **systematically study the effect of morphology on the CO₂ reduction reaction rate and selectivity**. After finding the optimal pore size, we also tuned the chemical properties of the N–C materials by changing the polymers precursor during synthesis. Our goal was to find a **correlation between the surface chemical composition, probed by XPS, and the CO₂ reduction activity**. It is known that the catalytic activity of N-doped carbon catalysts can be significantly improved by the incorporation of atomically dispersed metal centers. In light of this, we investigated **the effect of different metal centers on the CO₂ reduction and H₂ evolution activity of metal-nitrogen-doped carbon catalysts**.

2. Experimental techniques

The metal-free N–C catalysts were synthesized from conducting polymer precursors (polyaniline, polypyrrole, poly(o-phenylenediamine)) by high-temperature pyrolysis. During the synthesis of the porous samples we used silica nanoparticles with different pore sizes as templates (sacrificial support method). After pyrolysis the silica nanoparticles were etched out with hydrogen fluoride solution. The Mo–N–C catalysts were also synthesized by a sacrificial support method in the group of Prof. Plamen Atanassov (University of New Mexico, Center for Micro-Engineered Materials) using 4-aminoantipyrine and the appropriate metal-salt as the C- N- and metal precursors.

For the electrochemical measurements catalysts were spray-coated onto preheated glassy carbon plates with an Alder AD320 type airbrush and a custom-designed automated spray-coater equipment. The exact amount of catalyst coated was always weighed with a Mettler-Toledo XPE-26 microbalance.

Electrochemical measurements were performed using an Autalab PGSTAT204 potentiostat-galvanostat in a three-electrode configuration. The working electrodes were the catalyst-coated glassy carbon plates the counter electrodes were Pt disks and the reference electrode was a Ag / AgCl / 3 M NaCl electrode. Cyclic voltammograms (which we used for the determination of the electrochemically active surface areas) were recorded in a closed, one-compartment electrochemical cell. We studied the reduction activity of the catalysts by linear sweep voltammetry and chronoamperometry in a two-compartment closed electrochemical cell, in order to avoid product crossover between the two electrodes. The cathode and anode compartments were separated by a glass frit (linear voltammetry) or a Nafion 117[®] proton exchange membrane (chronoamperometry).

The products formed during CO₂ reduction were analyzed by gas chromatography (gas-phase) and ¹H NMR spectroscopy (liquid-phase). The cathode compartment of the electrolysis cell was directly connected to the injection unit of the gas chromatograph through a six-port valve, hence gas-phase products were analyzed *on-line*. We used a Shimadzu Tracera 2010 Plus gas chromatograph equipped with a barrier discharge ionization (BID) detector. For the product quantification, we calibrated the gas chromatograph using gas-mixtures (H₂, CO, CH₄, C₂H₄, N₂) with known concentrations in the 0,1 – 10 V / V% regime. ¹H NMR spectra were measured on a

500 MHz Bruker Avance instrument using a water-suppression method. Internal standards with known concentrations were used for the product quantification. During the isotopic labeling studies, we used a Shimadzu 2010 S type GC-MS instrument to follow the isotopic composition of CO and CO₂.

Raman spectra were recorded with a Senterra II Compact Raman microscope (Bruker) with 532 nm laser excitation, ≤ 2.5 mW power and 50x objective.

The morphology of the catalysts was studied by transmission (TEM) and scanning (SEM) electron microscopy. TEM pictures were taken with a FEI Technai G2 20X-Twin type instrument operating at an accelerating voltage of 200 kV. A Hitachi S-4700 field emission scanning electron microscope was used for the SEM measurements, operating at an accelerating voltage of 10 kV.

We recorded the N₂ adsorption / desorption isotherms of the catalysts using a Quantachrome Nova 3000e instrument at 77.4 K to determine the specific surface areas and the pore size distributions of the samples. Before the measurements, catalyst samples were pretreated at 200 °C in vacuum for two hours to remove all the adsorbed gases from the surface.

Surface chemical composition of the catalysts was measured by X-ray photoelectron spectroscopy (XPS). Measurements and analysis of the XPS spectra were performed by the group of Prof. Plamen Atanassov (University of New Mexico, Center for Micro-Engineered Materials) using a Kratos Axis Ultra DID spectrometer with monochromatic Al K α irradiation and the CasaXPS software.

Wetting properties of the catalyst layers were studied by measuring the dynamic advancing and receding contact angles. We used a Krüss GmbH EasyDrop instrument and ultrapure water as the test liquid. For the analysis, the DSA100 software was used.

The adsorption strength of CO₂ on the catalyst surfaces was determined by temperature programmed CO₂ desorption measurements using a BELCAT-A type instrument. After the pretreatment steps, CO₂ was adsorbed at 50°C on the samples for 30 minutes. The excess (not adsorbed) CO₂ was removed by rinsing with He. In the desorption step the catalysts were heated to 500 °C and the desorbed CO₂ was analyzed with a thermal conductivity detector.

In situ bubble formation during potentiostatic electrolysis was observed and recorded with a digital microscope (500x magnification) at different potentials for all studied samples. The size-

analysis of the bubbles right before their departure from the electrode surface was performed with the ImageJ image processing and analysis software.

3. Summary of new scientific results

Study of the CO₂ reduction mechanism by isotopic labeling experiments

T1. In a closed electrochemical cell with certain dimensions the dynamic equilibrium between gas-phase CO₂ and dissolved bicarbonate ions is not set instantaneously. Specifically, it took around two hours in our case.

According to this, if we perform CO₂ reduction in a selectively labeled CO₂ / HCO₃⁻ system (either the CO_{2,g}, or the HCO₃⁻,_{aq} is the ¹³C labeled compound), and follow the isotopic composition of the formed CO in time, we can decide whether it originated from the reduction of bicarbonate ions or the dissolved CO₂.

T2. During electrochemical CO₂ reduction the dissolved CO₂ is the actual reacting species at the surface of an N–C electrode, however, bicarbonate ions in the electrolyte play a key role in achieving selective CO-production.

In the selective isotopic labeling experiments, the isotopic composition the formed CO mirrored that of bicarbonate ions. In contrast, results of the control electrolysis experiments performed in electrolytes with different pH values suggested the direct reduction of CO_{2,aq}.pathway Taken together these findings, we concluded that CO_{2,aq} is converted directly at the electrode surface, however, the presence of bicarbonate ions in the electrolyte is essential in achieving high CO₂ reduction selectivity. Namely, bicarbonate ions act as a „CO₂-buffer” and quickly supply bicarbonate ions at the electrode surface through the HCO₃,_{aq}⁻ + H⁺ ⇌ CO_{2,aq} + H₂O equilibrium.

Effect of pore structure of N-doped carbon electrodes in the CO₂ reduction reaction

T3. We demonstrated, by systematic studies for the first time, that the CO₂ reduction selectivity of an N-doped carbon electrode can be increased by a factor of three only by introducing pores in the carbon structure. The optimal pore diameter appeared to be 27 nm in the studied pore size range.

We synthesized a model catalyst system in which the individual N–C samples were very similar in their physical-chemical properties and only differed in their porosity. This gave us a platform to systematically study the effect of morphology in the CO₂ reduction reaction. We could see a three-fold increase in the CO formation selectivity by introducing 27 nm diameter pores in the N–C

structure. The CO₂ reduction current and the selectivity increased in the order of 90 nm < 13 nm < 27 nm pore diameter through the porous catalysts.

T4. Superhydrophobic character, stronger CO₂ adsorption and higher curvature (smaller pore size) of the N–C catalysts resulted in better CO₂ reduction performance.

Superhydrophobic character of the porous catalysts favored CO₂ reduction vs. H₂ evolution, because of the suppression of water flooding in the pores. In case of the catalysts with smaller pores (27 nm and 13 nm) the shorter residence time and smaller size of the evolving gas bubbles during electrolysis resulted in increased mass transport, leading to the better CO₂ reduction performance of these samples. The CO₂ adsorption strength was highest in case of NC-27, which correlated with its highest CO₂ reduction activity. In addition, the samples with smaller pores having higher curvature and higher ratio of in-plane vs. edge defects could also play a role in their increased reduction performance.

Role of surface functional groups in the CO₂ reduction activity of N-doped carbon electrodes

T5. The N–C catalysts synthesized from different polymer precursors by the sacrificial support method differed in their chemical composition which resulted in variations in their CO₂ reduction performance. The CO partial current densities increased with the increasing N-content of the catalysts, except in case of the NH₃ post-treated sample.

The N-content of the N–C catalysts prepared from different conducting polymer was between 4 and 8 atomic% and was in line with the N-content of the precursor polymers. Samples for which the polymer precursor was rich in poly(o-phenylenediamine) had the highest CO₂ reduction activity and selectivity, because of the higher N-contents. The NH₃-treatment slightly increased the activity and selectivity of the bare PoPD-C, while with the KOH treatment both decreased drastically.

T6. In the thermally activated CO₂ hydrogenation reaction the same products (CO and CH₄) were formed as in the electrochemical CO₂ reduction on the studied N–C catalysts. The trend in the activity of the catalysts was the same in the electrochemical and thermochemical reaction, indicating that the identity of catalytic centers is very similar in the two processes.

The catalysts prepared from different polymer precursors were also investigated in the heterogenous catalytic hydrogenation of CO₂. CO was the main reduction product, and CH₄ also

formed in minor amounts, similarly to the electrochemical reaction. The CH₄ / CO molar ratio was around one order of magnitude higher in the thermally activated reaction than in the electrochemical reduction. This was most probably because of the absence of H₂ evolution in the prior case. In the thermally activated reaction, the same catalysts were found to be the most active as in the electrochemical reduction, suggesting the similar role of the surface functional groups in the two cases.

Investigation of metal-nitrogen doped catalysts in the CO₂ reduction and H₂ evolution reactions

T7. The different metal ions present during the synthesis of the M–N–C catalysts affected the physical-chemical properties of the N–C structure. As a result of this, both the surface area and the N-content of the metal-containing samples increased compared to the metal-free catalyst.

The different metal salts in the precursor mixture changed the physical-chemical properties of the N-C structure during pyrolysis. The total N-content varied between 2 and 6 atomic%, being the smallest for the metal-free (2,6 %) and highest for the Cu-containing (5,8 %) sample. The electrochemical surface area increased by a factor of two in case of the Mo–N–C sample, compared to the metal-free N–C catalyst.

T8. The incorporation of metals in the N-doped carbon structure increased the total reduction activity but decreased the CO₂ reduction selectivity for each studied metal (Cu, Ce, Mo, Pr).

While the reduction currents only slightly increased in case of Pr–N–C and Ce–N–C, a drastic increase could be observed for Cu–N–C and Mo–N–C. This activity-improvement was the result of the increased H₂ evolution, while the CO₂ reduction activity decreased in case of all studied metals. The partial current density of H₂ correlated with the total metal- and pyridinic N-content of the samples.

4. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10054957

Publications related to the scientific topic of the dissertation:

1. **D. Hursán**, A.A. Samu, L. Janovák, K. Artyushkova, T. Asset, P. Atanassov, C. Janáky: Morphological attributes govern carbon dioxide reduction on N-doped carbon electrodes
Joule, **2019**, 3, 1719-1733.
2. A. Roy, **D. Hursán**, K. Artyushkova, P. Atanassov, C. Janáky, A. Serov: Nanostructured metal-N-C electrocatalysts for CO₂ reduction and hydrogen evolution reactions
Appl. Catal. B Environ., **2018**, 232, 512–520. **IF₂₀₁₈= 14.229**
3. **D. Hursán**, C. Janáky: Electrochemical reduction of carbon dioxide on nitrogen-doped carbons: Insights from isotopic labeling studies
ACS Energy Lett., **2018**, 3, 722–723. **IF₂₀₁₈=16.331**

ΣIF=30.560

Other publications:

- A. Kormányos, **D. Hursán**, C. Janáky; Photoelectrochemical behavior of PEDOT/nanocarbon electrodes: Fundamentals and structure–property relationships
J. Phys. Chem. C., **2018**, 122, 13682-13690. **IF₂₀₁₈= 4.309**
- D. Hursán**, G. London, B. Olasz, C. Janáky; Synthesis, characterization , and electrocatalytic properties of a custom-designed conjugated polymer with pyridine side chain
Electrochim. Acta., **2016**, 217, 92–99. **IF₂₀₁₆ = 4.798**
- D. Hursán**, A. Kormányos, K. Rajeshwar, C. Janáky; Polyaniline films photoelectrochemically reduce CO₂ to alcohols
Chem. Commun., **2016**, 52, 8858–8861. **IF₂₀₁₆ = 6.319**
- C. Janáky, D. Hursán**, B. Endrődi, W. Chanmanee, D. Roy, D. Liu, NR De Tacconi, B.H. Dennis, K. Rajeshwar; Electro- and photoreduction of carbon dioxide: The twain shall meet at copper oxide / copper interfaces
ACS Energy Lett., **2016**, 1, 332–338. **IF=12.277**
- B. Endrődi, **D. Hursán**, L. Petrilla, G. Bencsik, C. Visy; Incorporation of cobalt-ferrite nanoparticles into a conducting polymer in aqueous micellar medium: Strategy to get photocatalytic composites
Acta Chimica Slovenica, **2014**, 61, 376-381. **IF₂₀₁₄ = 0.686**

ΣΣIF=46.672

Oral presentations

Presenting author:

D. Hursán, A.A. Samu, K. Artyushkova, P. Atanassov, C. Janáky: CO₂ conversion on N-doped carbon electrodes: Morphological and mechanistic insights
American Chemical Society National Meeting & Exposition, Orlando (FL, USA), 31 March - 4 April, 2019.

D. Hursán, A.A. Samu, C. Janáky: Electrochemical reduction of CO₂ on N-doped carbon electrodes: understanding mechanism and the role of morphology
Szeged International Workshop on Advances in Nanoscience, Szeged (Hungary), 7-10, October, 2018.

D. Hursán, A.A. Samu, C. Janáky: Mechanistic and morphological insights into the CO₂ electroreduction on N-doped carbon electrodes, International Symposium on Electrocatalysis, Szczyrk (Poland), 1. September – 29. August, 2018.

D. Hursán, A. Kormányos, C. Janáky: Photoelectrochemical fuel generation using organic semiconducting polymer photoelectrodes,
XL. Kémiai Előadói Napok, Szeged (Hungary), 16-18, October, 2017.

D. Hursán, A. Kormányos, T. Kiss, C. Janáky: Solar fuel generation using organic semiconducting polymer photoelectrodes, 68th ANNUAL Meeting of the International Society of Electrochemistry, Providence (RI, USA), 1. September - 27. August, 2017.

D. Hursán, A. Kormányos, T. Kiss, G. London, C. Janáky: Photoelectrochemistry of conducting polymers and opportunities in solar fuel generation, 254th American Chemical Society National Meeting & Exposition, Washington DC (USA) 20-24, August, 2017.

D. Hursán, A. Kormányos, T. Kiss, G. London C. Janáky: Photoelectrochemistry of organic semiconducting polymers: fundamentals and implications in solar fuel generation, 21st Topical Meeting of the International Society of Electrochemistry, Szeged, (Hungary), 23-26, April, 2017.

D. Hursán, C. Visy, C. Janáky: CO₂ fotoelektrokémiai átalakítása tüzelőanyagokká vezető polimer elektródokon XXXVII. Kémiai Előadói Napok, Szeged (Hungary), 3-5, November, 2014.

Co-author:

A. Kormányos, **D. Hursán**, C. Janáky: Photoelectrochemical Reduction of CO₂ on Organic / Inorganic Nanocomposite Photoelectrodes, 21st Topical Meeting of the International Society of Electrochemistry, Szeged (Hungary), 23-26, April, 2017.

A. Kormányos, **D. Hursán**, K. Rajeshwar, C. Janáky: Photoelectrocatalytic reduction of CO₂ on organic/inorganic nanocomposite photoelectrodes, 253rd ACS National Meeting and Exposition, San Francisco (USA), 2-6, April, 2017.

B. Endrődi, **D. Hursán**, E. Kecsenovity, K. Rajeshwar, C. Janáky: Nanostructured hybrid electrodes for photoelectrochemical CO₂ conversion: synthetic aspects and structure-property relationships, 5th International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Porto Heli (Greece), 26-30, June, 2016.

C. Janáky, A. Kormányos, **D. Hursán**, K. Rajeshwar: Photoelectrochemical reduction of CO₂ on hybrid organic/inorganic photocathodes, ACS National Meeting and Exhibition, San Francisco (USA), 10-14, August, 2014.

Poster presentations:

D. Hursán, G. London, C. Janáky: Electrochemical reduction of carbon dioxide on N-doped carbon electrodes: Morphological and mechanistic aspects
69th Meeting of the International Society of Electrochemistry, Bologna (Italy), 2-7, September, 2018.

D. Hursán, A. Kormányos, T. Kiss, G. London, C. Janáky: Photoelectrochemistry of conducting polymers and opportunities in solar fuel generation
254th American Chemical Society National Meeting & Expo, Sci-Mix, Washington DC (USA) 20-24, August, 2017.

D. Hursán, B. Olasz, G. London, C. Janáky: Custom-designed Electroactive Polymers for H₂ evolution and CO₂ Reduction
67th Annual Meeting of the International Society of Electrochemistry, The Haage (Netherlands), 21-26, August, 2016.

D. Hursán, A.A. Samu, C. Janáky: Electrocatalytic CO₂ Reduction on a Copper Decorated Hierarchically Porous Graphitic Carbon
International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems, Porto Heli (Greece), 26-30, June, 2016.

D. Hursán, B. Olasz, G. London, C. Janáky: Electrodeposition of Molecularly Engineered Conducting Polymers for the electroreduction of CO₂, *11th International Workshop of Electrodeposited Nanostructures*, Balatonfüred (Hungary), 10-11, September, 2015.

D. Hursán, B. Olasz, G. London, C. Janáky: Electrochemical Synthesis and Characterization of New Polyaniline-Based Materials for CO₂ Capture and Conversion, Workshop on the Electrochemistry of Electroactive Materials, Bad Herrenalb (Germany), 31 May- 5 June, 2015.