Doctoral (Ph.D.) Thesis

Nitrogen doped graphene supported oxygen reduction reaction catalysts

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1. Introduction and aims

The growing population of Earth requires more and more energy. However, a large part of this energy is produced from fossil fuels that are non–renewable resources and their amount is shrinking rapidly. In order to address this energy consumption problem, many researchers investigate alternative ways that can help in our future.

There are many alternative ways to solve these problems. One of them is to use fuel cells that convert chemical energy into electrical energy during the oxidation of the fuel. The anode and cathode side of the system are separated by an electrically insulating membrane. Electrons produced by the oxidation of the fuel (hydrogen gas, methanol, ethanol, formic acid, glycerin, ethylene glycol etc.) reach the cathode side by using an outer circle where the reduction of oxygen takes place. Depending on the type of fuel cell, the ions required for the process can cross the membrane to reach the anode or the cathode side. Proton exchange membranes are usually made from a sulfonated polytetrafluoroethylene called Nafion®, which is patented by DuPont. The ion conductivity of anion exchange membranes is usually lower compared to proton exchange membranes. However, this difference decreased significantly recently. The most commonly used anion exchange membranes are produced by Tokuyama and Fumatech.

Conventional fuel cells are not very competitive today commercially because of the high price of the platinum catalyst placed on the anode and cathode side. Furthermore, platinum-based systems suffer rapid activity loss due to catalyst degradation. Therefore, it would be important to reduce the amount of the precious metal, increase the durability of the catalyst, or replace it with cheaper composite alternatives.

The so-called noble-metal-free catalysts could be promising for catalyzing the oxygen reduction (ORR) process on the cathode side. In non-noble metal catalysts, different transition metals and their oxides, nitrides, carbides or sulfides could replace the noble metals. According to the previous literature data, different compounds of iron and cobalt are considered to be the most suitable ORR catalysts.

The other group of noble-metal-free catalysts is that of the so-called metal free catalysts, which are usually various carbon structures doped with heteroatoms. Besides their electrocatalytic activity, they can also be used as a support, thus making it possible to make more effective composites.

The aim of my research was the preparation of catalysts efficient in the oxygen reduction reaction. In order to reach this goal, nitrogen doped graphene was used as a support. Three different catalyst types were prepared in which the other component of the composite was platinum, cobalt nitride or iron nitride. Nitrogen doped graphene, and the platinum particles or the transition metal nitrides were simultaneously formed during the synthesis.

The platinum containing samples had the same composition but their annealing temperatures were different. The oxygen reduction activity of the as–prepared composites was tested in acidic as well as in alkaline media to find the one most suitable for proton exchange or anion exchange membrane fuel cells. The annealing temperature was the same in all transition metal nitride containing samples but their compositions were different. The electrocatalytic activity was tested only in alkaline media because of the poor activity of the non-noble metals in low pH electrolyte.

2. Experimental methods

The following method was used to prepare the composites. A calculated amount of the precursor salt of the particle was added to the suspension of graphene oxide prepared by a modified Hummers method. After 24 hours of stirring the solution was freeze dried. The dry powder was annealed in ammonia atmosphere, where nitrogen doped graphene and – depending on the precursor salt – platinum, cobalt nitride or iron nitride particles were formed simultaneously. The morphology of nitrogen doped graphene and the composites, as well as the size distribution of the particles was determined using a FEI Tecnai G2 20 X-Twin transmission electron microscope (TEM). Crystalline structure was investigated with a Rigaku Miniflex II x-ray diffractometer (XRD) operating with a CuKα (λ = 0,154 nm) X-ray source. A Thermo Scientific DXR Raman microscope was used for the Raman spectroscopic measurements utilizing a 532 nm laser excitation at 5 mW power. Elemental composition was investigated by a SPECS X-ray photoelectron spectroscope equipped with a PHOIBOS 150 MCD 9 hemispherical analyzer.

A GILL AC galvanostat-potentiostat was used for the investigation of the oxygen reduction activity. The measurements were carried out in a classic three electrode system where the working electrode was a glassy carbon rotating disk electrode measuring 3 mm in diameter, which was modified on its surface with our catalysts. The auxiliary electrode was a platinum wire, while an Ag/AgCl/3M NaCl (E = 0,209 V vs RHE) served as the reference electrode. Cyclic and linear sweep voltammetry measurements (CV and LSV) were taken in 0.1 M perchloric acid and in 0.1

M potassium hydroxide solution if the catalyst contained platinum, while only alkaline media was used when testing non-noble metal composites. Depending on the measurement, the electrolytes was bubbled with nitrogen or oxygen gas before the recording of the voltammograms. Methanol tolerance was tested by chronoamperometry measurements. 1 cm^3 of 3 M methanol solution was added to the system at a given time of the measurement, then we determined the effect of methanol on the measured current for the catalyst investigated.

3. Summary of new scientific results

One step synthesis and investigation of platinum decorated nitrogen doped graphene composite

T1. We have developed a simple method to prepare a composite containing nitrogen doped graphene and platinum nanoparticles dispersed on its surface. During this process, platinum(II)-acetylacetonate was added to a graphene oxide solution. The mixing was followed by freeze drying and the powder mixture was annealed in ammonia. Morphological properties were studied by using transmission electron microscopy (TEM) while the elemental composition was investigated by X-ray photoelectron spectroscopy.

T2. We proved by TEM measurements, that the applied heat treatment temperature affects the average particle size: it was 3-4 nm in case of 500 and 600 °C, while 6.2 nm was the average diameter when samples with 10 wt% platinum content were annealed at 700 °C. The average size of the particles formed during the synthesis was close to the 2-3 nm range which is optimal for oxygen reduction reaction. The structure of graphene was visibly degraded at the latter temperature according to the TEM images.

T3. Using the Pt 4f signal, we proved by X-ray photoelectron spectroscopy that the as-prepared composites contain platinum in +2 and +4 oxidation states besides the zero valent form. We suggested two possible explanations for this: (i) the high surface atom percentage of the particles can interact with the oxygen molecules of the air, and/or (ii) graphene has higher electronaffinity close to the polar moieties formed during the doping process. This can improve electron donation from the platinum nanoparticles, which results in a stronger interaction between the support and the particles.

Oxygen reduction activity of platinum decorated nitrogen doped graphene composite in acidic and in alkaline media.

T4. We showed by linear sweep voltammetry measurements, that higher activity was reached in case of the composites prepared in 500 and 600 °C when 0.1 M perchloric acid was used, while better performance was achieved with the composite annealed at 700 °C when the electrolyte was 0.1 M potassium hydroxide. The activity was determined based on the onset potentials and the reduction current densities (taken at 0.1 V vs RHE) of the linear sweep voltammetry measurement and the electron transfer numbers determined by using the Koutecky-Levich equation

Synthesis and investigation of transition metal nitride/nitrogen doped graphene composites.

T5. We developed a simple method where the composite of Co_4N particles and nitrogen doped graphene was formed by annealing the mixture of cobalt(II)-acetate and graphene oxide in ammonia atmosphere. We showed that the average particle size of the cobalt nitride particles increased with the cobalt content as 14.3 ± 7.1, 43.1 ± 17.4, and 205.2 ± 165.9 nm in case of 5, 10, and 20 wt% Co, respectively. Morphological and structural properties were determined by using transmission electron microscopy, X-ray diffractometry, and X-ray photoelectron spectroscopy.

T6. We used a similar method to prepare a nanocomposite featuring a mixture of FeN and Fe_2N particles dispersed on the surface of nitrogen doped graphene. The composite was formed during the ammonia treatment of the mixture of iron(III)-acetylacetonate and graphene oxide. We proved that the average particle size of the iron nitride particles increased with the iron content as 23.4 ± 9.2, 78.2 ± 33.6, 105.1 ± 56.4, and 127.0 ± 41.8 nm in case of 5, 10, 20 and 50 wt% Fe, respectively. Morphological and structural properties were determined by using transmission electron microscopy, X-ray diffractometry and X-ray photoelectron spectroscopy.

T7. We proved by XPS measurements, that the nitrogen/carbon atomic ratio is controllable in the support of the composite contains nitrogen doped graphene and transition metal nitrides. The results revealed that this ratio was increased from 0.062 to 0.086 upon increasing the cobalt content up to 10 wt%. Any further increase of the transition metal content did not alter the ratio significantly. However, even higher nitrogen/carbon atom ratios were reached in samples containing iron nitride. The ratio increased from 0.098 to 0.122 when increasing the iron content from 5 to 20 wt%. Further increase in the transition metal content did not cause any further improvement in the N/C ratio.

Oxygen reduction activity of transition metal nitride/nitrogen doped graphene composites in alkaline media.

T8. We found by studying the oxygen reduction activity of samples containing cobalt nitride that the onset potential of the linear sweep voltammograms was shifted to a more positive value when decreasing the particle size. This means that the activity can be improved by decreasing the particle size. In contrast, there was no significant difference between the onset potentials of the iron nitride/nitrogen doped graphene samples in case of 5, 10 and 20 wt% iron content, while it was a more negative value in case of 50 wt%.

T9. We proved by rotating disk electrode measurements of Co_4N/NG samples, that the composite with 10 wt% cobalt content has the highest activity towards oxygen reduction reaction. We gave the following explanation for this result. The nitrogen content of the support was higher in case of 10 wt% Co, which could cause a higher activity of the support and also of the composite compared to the 5 wt% sample even if the particle size was bigger. Furthermore, we proved that the properties of our composites are close to the electrocatalytic activity of the most commonly used amorphous carbon supported platinum nanoparticles. The electrocatalytic activity was determined based on the reduction current densities (taken at 0.0 V vs RHE) of the linear sweep voltammograms of Co_4N/NG samples, and the electron transfer numbers determined by using the Koutecky-Levich equation.

T10. We proved by rotating disk electrode measurements of the FeN_x/NG samples, that the composite with 20 wt% iron content showed the highest activity in oxygen reduction reaction. We gave the following explanation for the result. The support has higher nitrogen content, which could cause a higher activity of the support and also of the composite even if the particle size was bigger than in case of 5 and 10 wt%. The electrocatalytic activity was determined based on the reduction current densities (taken at 0.0 V vs RHE) of the linear sweep voltammograms of FeN_x/NG samples, and the electron transfer numbers were determined by using the Koutecky-Levich equation.

T11. We proved by methanol tolerance measurements, that the activity of our non-noble metal catalysts does not change in the presence of methanol. In contrast, the most commonly used platinum catalyst suffered a 60% activity loss under the same conditions. We explain this by the fact that platinum catalyzes the methanol oxidation process as well, which results in a smaller number of active sites remaining available for the oxygen reduction.

4. List of publications

Hungarian Scientific Bibliography (MTMT) identifier: 10055199

Publications related to the present thesis

1. Tamás Varga, Ágnes Timea Varga, Gergő Ballai, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya
One step synthesis of chlorine-free Pt/Nitrogen-doped graphene composite for oxygen reduction reaction
CARBON 133: pp. 90-100. (2018)
IF: 7.082

2. Tamás Varga, Gergő Ballai, Lívia Vásárhelyi, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya
Co_4N/nitrogen-doped graphene: a non-noble metal oxygen reduction electrocatalyst for alkaline fuel cells
APPLIED CATALYSIS B-ENVIRONMENTAL 237: pp. 826-834. (2018)
IF: 11.698

3. Tamás Varga, Lívia Vásárhelyi, Gergő Ballai, Henrik Haspel, Albert Oszkó, Ákos Kukovecz, Zoltán Kónya
Noble-Metal-Free *Iron Nitride/Nitrogen-Doped Graphene Composite for the Oxygen Reduction Reaction*
ACS OMEGA 4 : 1 pp. 130-139., 10 p. (2019)
IF: -

Conferences

Oral presentations

1. Tamas Varga, Henrik Haspel, Ákos Kukovecz, Zoltán Konya

Synthesis, characterisation, and electrochemical properties of graphite oxide/vanadate nanowire composites

The Eleventh Conference for Young Scientists in Ceramics, SM-2015, 21- 24. October 2015, Novi Sad.

2. Tamás Varga, Henrik Haspel, Zoltán Kónya

Structural and electrochemical properties of NH_3 treated tungsten oxide nanowires

A Magyar Mikroszkópos Társaság éves konferenciája, MMT 2016, 19- 21. May 2016, Siófok.

3. Tamás Varga, Henrik Haspel, Zoltán Kónya

Structural, morphological and electrochemical properties of NH_3 treated tungsten oxide nanowires

Young Investigators' Seminar on Analytical Chemistry, YISAC 2016, Novi Sad, 18. June- 01. July 2016, Novi Sad.

4. Tamás Varga, Gergő Ballai, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya

Non-noble metal catalyst and its oxygen reduction reaction activity

A Magyar Mikroszkópos Társaság éves konferenciája MMT 2018, 24- 26. May 2016, Siófok.

5. Tamás Varga, Gergő Ballai, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya

A kobalt-nitrid/nitrogénnel adalékolt grafén kompozitok összetételének oxigénredukciós aktivitásra gyakorolt hatása

PhD hallgatók anyagtudományi napja, 26. November 2018, Veszprém.

Poster presentations

1. Tamás Varga, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya,
Synthesis and characterisation of graphite-oxide/vanadate nanowire composites
NanoPortugal International Conference, nanoPT 2015, Porto, 11- 13. February 2015, Porto.

2. Tamás Varga, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya
Synthesis of highly photoactive tungsten nitride nanosheets by ammonia treatment of tungsten oxide nanowires
7th Szeged International Workshop on Advances in Nanoscience 2016, SIWAN7, Szeged, 12- 15. October 2016, Szeged.

3. Tamás Varga, Attila Kormányos, Henrik Haspel, Csaba Janáky, Ákos Kukovecz, Zoltán Kónya
Synthesis and structural investigation of tungsten oxynitride and tungsten nitride nanostructures
21st Topical Meeting of the International Society of Electrochemistry, Topical 21, Szeged, 23- 25. April 2017, Szeged.

4. Ágnes Timea Varga, Tamás Varga, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya
One step synthesis of Pt/Nitrogen-doped graphene composite for oxygen reduction raction
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5. Gergő Ballai, Tamás Varga, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya

Oxygen reduction activity of cobalt-nitride on nitrogen-doped graphene
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7. Krisztina Anita Nagy, Gergő Ballai, Ágnes Timea Varga, Tamás Varga, Henrik Haspel, Ildikó Y. Tóth, Ákos Kukovecz

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8. Gergő Ballai, Tamás Varga, Lívia Vásárhelyi, Henrik Haspel, Ákos Kukovecz, Zoltán Kónya

Electrocatalytic activity of Co_4N/nitrogen-doped graphene composites in the oxygen reduction eaction

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9. Lívia Vásárhelyi, Tamás Varga, Gergő Ballai, Henrik Haspel, Albert Oszkó Ákos Kukovecz, Zoltán Kónya

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8th Szeged International Workshop on Advances in Nanoscience, SIWAN8, 7- 10. October 2018, Szeged.

12. Imre Szenti, András Sápi, Upendar Kashaboina, Juan Fernando Gomez Perez, Gyula Halasi, János Kiss, Tamás Varga, Ákos Kukovecz, Zoltán Kónya

Controlled sized platinum nanoparticles supported on H-ZSM-5 catalyst for efficient CO_2 hydrogenation: role of interfacial sites in high activity

8th Szeged International Workshop on Advances in Nanoscience, SIWAN8, Szeged, 7- 10. October 2018.

Other publications

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***SURFACE SCIENCE* 648:** pp. 114-119. (2016)

IF: 2.062

2. Balázs Zsirka, Erzsébet Horváth, Péter Szabó, Tatjána Juzsakova, Róbert K Szilágyi, Dávid Fertig, Éva Makó, Tamás Varga, Zoltán Kónya, Ákos Kukovecz, János Kristóf

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IF: 4.439

3. Tamás Varga, Henrik Haspel, Attila Kormányos, Csaba Janáky, Ákos Kukovecz, Zoltán Kónya

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IF: 2.067

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SCIENTIFIC REPORTS 8:(1) p. 3943. 12 p. (2018)
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IF: 2.801

Peer-reviewed papers total: 10	out of this, related to the topic of this thesis: 3
Cumulative impact factor: 43,9	out of this, related to the topic of this thesis: 18,78
Independent cites total: 42	out of this, related to the topic of this thesis: 11