Mechanical, electrical and wetting properties of porous, carbon-based structures

Doctoral (Ph.D.) Thesis

Krisztina Anita Nagy

Supervisors: Dr. Ákos Kukovecz, associate professor
Dr. Ildikó Vidákné Tóth, assistant professor

Doctoral School of Environmental Science

Department of Applied and Environmental Chemistry
University of Szeged
Faculty of Science and Informatics

Szeged
2021

1. Introduction and aims

Numerous environmentally damaging processes take place in our fast-paced world. Air pollution, caused to some extent by increasing CO_2 emissions, is one of them. Furthermore, water pollution is another significant problem, e.g. oil spills on the water. Some carbon-based structures, like carbon nanotubes or carbon fibre based gas diffusion layers can contribute to solving these issues in a direct or indirect manner. We have chosen to work with carbon nanotubes to make them even better known to the scientific community and potentially open up new avenues for their use. I prepared carbon nanotube films („buckypapers”) by filtration, then designed and built a system capable of recording the electrical response of porous materials (including buckypapers) under compression load. Further considering the application of carbon nanotubes, functionalized carbon nanotubes/nonwoven textile composites were also prepared by filtration. These may be used in water treatment, due to their tuneable surface wetting properties.

Reducing air pollution by using fuel cells to replace fossil fuels is an attractive research topic today. Fuel cells are electrochemical cells that can convert chemical bonding energy to electricity directly. A necessary part for their operation are the so-called gas diffusion layers, which consist of mostly carbon fibres and a microporous layer. These ensure the free flow of gases and by-products. It is important to know the hydrophilic–hydrophobic behaviour of the gas diffusion layers for their optimal operation. We have obtained information about the wetting properties of gas diffusion layers by *ex situ* methods. Compression of gas diffusion layers in the fuel cells ensures the proper contact required for good electrical conductivity. Therefore, we utilized the instrument built for testing electrical conductivity under mechanical load to assess the compression-dependent electrical resistance of gas diffusion layers just as we tested carbon nanotube films previously. This way we gained knowledge in an *ex situ* manner on processes that also take place in the fuel cell.

2. Experimental and methods

Multi-walled carbon nanotube films (CNT film) were prepared by vacuum filtration from non-functionalized carbon nanotubes (nfCNT) previously synthesised by the CCVD (*catalytic chemical vapour deposition*) method. Non-functionalized carbon nanotubes were suspended in dimethyl-formamide for filtration, then filtered into buckypapers of equal diameter but increasing weight (6, 8 10, 18 mg). 3-3 pieces were produced for each mass.

Films were prepared from carboxy-functionalized carbon nanotubes (fCNT) in a similar way using vacuum filtration, but deionized water was employed as a dispersing medium in this case and the buckypaper weight was fixed at 10 mg. The carboxy-functionalized carbon nanotubes/nonwoven textile (fCNT/NW) composites were also prepared by vacuum filtration. The nonwoven textile was a needle-punched fabric made of polyester fibres. A piece of NW textile with almost the same diameter as the inner cross-section of the filter funnel was cut, and the fCNT–water suspension was filtrated through the fabric.

Certain structural parameters of nfCNT and fCNT were determined by FEI TECNAI G^2 20 X-Twin transmission electron microscope by using 200 kV accelerating voltage. Morphological characterization of our materials (CNT films, fCNT/NW composites, and the gas diffusion layer (GDL)) was performed by a Hitachi S-4700 Type II cold cathode field emission scanning electron microscope. The absolute density of multi-walled carbon nanotubes was measured by a Micrometrics Multi Volume Pycnometer 1305 type gas pycnometer. Further morphological parameters and the porosity of the carbon cloth type gas diffusion layer were observed using a Bruker Skyscan 2211 X-Ray nanotomograph. The two different surfaces of the GDL were examined by a Veeco Detak8 Advanced Development Profiler® contact profilometer.

Optical contact angle measurements were carried out at room temperature (~25 °C). The volume of the water droplet was 10 μL (coloured with methylene blue for better visibility) in case of fCNT/NW samples. The water/or water–alcohol mixture droplet was 5 μL in case of GDL sample. Contact angle measurements were performed using a Dino-Lite Edge type digital microscope and evaluated using the *ImageJ*® software.

A multifunctional instrument capable of monitoring the evaporation of sessile, microliter liquid droplets was used to study the evaporation of liquids on GDL. The sample was lain on the sample holder while the droplet (5 μL) was placed on the middle of the sample. The evaporation was monitored from top view by a FLIR A655sc type infrared camera. The sample holder stood on a Sartorius Cubis MSU225S-000-DU type analytical balance that can register the weight loss of droplets during evaporation. Our experiments were carried out at 60 °C, which means that starting temperature of the solid sample was 60±2 °C. Temperature control was ensured by a Peltier heater, which was a separate unit under the sample holder.

A new instrument was developed in my doctoral work for load-dependent electrical resistance measurements. This can record electrical resistance changes during the compression of the material. It has a stable scaffold with 21 cm of height and 20 cm of diameter. Further parts of the instrument are a micrometer screw (first a Moore and Wright Electronic Outside Micrometer was used, which was replaced later by a Mitutoyo micrometer screw); exchangeable load cells: Futek LLB130 50 lb (~222 N) and LLB130 5 lb (~22 N); and 2 copper electrodes (d= 15 mm). The latter ensure two-point electrical resistance measurements and the bottom electrode doubles as sample holder too. The force exerted on the sample is provided by moving the top electrode, which can be done by twisting the micrometer screw. Further parts of the system are the mechanically stable ceramic tiles. They cannot be compressed under the forces we used, and they are electrical insulators. The top electrode was fixed to the upper ceramic tile with the help of a screw, while the bottom electrode was not immobilized to the lower ceramic plate. Thus it doesn't hold it, that is why it doesn't disturb the load measurements. Copper wires are attached to both the bottom and top electrodes to ensure the contact between the electrodes and the data logger. The load cell is placed under the lower ceramic plate and the bottom electrode. Since the load sensor is made from metal, we needed to use a 3 mm thick glass plate to insulate the bottom electrode and the load cell. The signal processing unit of the pressure sensor is a Futek IPM650 type intelligent panel mount. Electrical resistance measurements were first carried out by a Voltcraft VC920 digital multimeter, which was later replaced by a National Instruments (NI) USB-6003 type data logger.

3. Summary of new scientific results

Methods developed to investigate the electrical and wetting properties of porous structures

T1. We were the first to apply *ex situ*, simultaneous measurement techniques to determine the wetting and evaporation properties on carbon cloth type gas diffusion layer for different liquids. The experimental system consisted of an infrared camera, an analytical balance, and a sample holder placed on the balance. Furthermore, optical contact angles were also investigated by a digital microscope.

T2. We designed and built an instrument for recording the electrical resistance changes during the mechanical compression of fibrous conducting films. It consists of a lower copper electrode and a movable upper electrode. The movement is ensured by a micrometre screw. The micrometre screw doubles as an accurate displacement measuring device. The mechanical pressure is measured by a load cell (pressure sensor). Electrical response is obtained from the electrical resistance of the sample, which is measured between the two electrodes.

Studies on functionalized carbon nanotubes/nonwoven textile composites with tuneable wetting properties

T3. We were the first to produce composites consisting of carboxy-functionalized carbon nanotubes and nonwoven textile containing polyester fibres (nominal carbon nanotube loading: 0; 5; 10 and 15 weight%) by filtration. Filtration technique results in composites with a layered structure, where a part of the carbon nanotube is concentrated on the top of the fabric. The morphology of samples containing different amounts of carbon nanotubes was observed by scanning electron microscopy. Furthermore, we determined the volume fraction of carbon nanotubes in the composites (0; 0,06; 0,19 and 2,3 %) from the scanning electron microscopy images.

T4. We verified a literature model with contact angle measurements where carbon nanotube/textile composites exhibited improving wetting properties with increasing carbon nanotube content compared to hydrophobic, pure nonwoven fabrics. The starting contact angles of 0–15 weight% samples were between 132,8°and 51,9° and exhibited a decreasing trend that matched the values predicted by the model well. We proved with experiments that the hydrophilic–hydrophobic properties can be tuned by varying the amount of carbon nanotubes in the composite.

Surface wetting and evaporation properties of different solvents on carbon cloth type gas diffusion layer

T5. Water evaporating from a carbon cloth type gas diffusion layer exhibits a non-linear weight loss trend. We proved that this correlates with the hydrophobic property ($\Theta > 90°$) of the layer. We monitored the evaporation of water droplet (starting contact angle ~135°) using weight loss measurements. We identified from the slope of the weight loss curves that the first section is faster (~0,015-0,017 mg/s) than the second part (~0,012 mg/s) of the evaporation on both sides of the carbon cloth. The first part lasts until the droplet contact angle reaches 90°. Evaporation has a decreasing rate, which indicates the hydrophobic nature of the sample.

T6. We demonstrated that the wettability of the gas diffusion layer improves with increasing alcohol content in ethanol/methanol – water mixtures. This observation was based on infrared thermography and contact angle measurements. We observed improving wettability with increasing alcohol content (0→100 weight%) reinforced by the decreasing starting contact angles (~135→0°) and droplet/wetted area (~4→30 mm^2).

Investigation of electrical response of porous carbon based structures under mechanical load

T7. We verified a literature model with a series of experiments, which claims, that the volume fraction of self-supporting films filtrated from carbon nanotubes has an effect on the piezoresisitive properties of the films. The electrical resistance of the films (6; 8; 10; 18 mg of nfCNT) was decreasing (~4→0.2 Ohm) under compression.The reasons behind this phenomenon are that the film is more compact (volume fraction: ~0,03→0,08), and the number of contact points between the nanotubes increases upon compression.

T8. We demonstrated that carbon cloth type gas diffusion layers behave similarly to self-supported carbon nanotube films in terms of mechanical loading – electrical response. The electrical resistance of gas diffusion layers decreased under compression, which corresponds well with the model already mentioned in T7.

Opportunities of practical application

The materials presented here can play a significant role in environmental protection because they possess useful characteristics like porosity and good mechanical properties. Carbon nanotubes have been used in sensors for a long time, but in the form of self-supporting materials e.g. films or sponges they have also exceptional applicability in the field of water treatment. We think that the carbon nanotube/nonwoven textile composites put forth here can have a role in water treatment in the future due to their porous structure and tuneable wettability. Gas diffusion layers play an indisputable role in environmental protection as fuel cell components. We demonstrated that *ex situ* experiments can be used to determined some important gas diffusion layer characteristics faster and more cost effectively than alternative methods. These developments can be significant in developing fuel cells in the future.

4. List of publications

Hungarian Scientific Bibliography (MTMT) identifier: 10054989

Publications related to the present thesis

1. Vijay Kumar, Henrik Haspel, Krisztina Nagy, Amit Rawal, Ákos Kukovecz
Leveraging compressive stresses to attenuate the electrical resistivity of buckypaper
CARBON 110: pp. 62-68. (2016)
IF_{2016}: 6.918

2. Krisztina Nagy, Krishn Gopal, Rajput, Ildikó Y. Tóth, P.V. Kameswara Rao, Sumit Shamra, Vijay Kumar, Amit Rawal, Ákos Kukovecz
Self-similar arrays of carbon nanotubes and nonwoven fibers with tunable surface wettability
MATERIALS LETTERS 228: pp. 133-136 (2018)
IF_{2018}: 3.252

3. Krisztina Anita Nagy, Ildikó Y. Tóth, Gergő Ballai, Ágnes Timea Varga, Imre Szenti, Dániel Sebők, Judit Kopniczky, Béla Hopp, Ákos Kukovecz
Wetting and evaporation on a carbon cloth type gas diffusion layer for passive direct alcohol fuel cells
JOURNAL OF MOLECULAR LIQUIDS 304: pp. 112698 (2020)
IF_{2019*}: 5.358

Cumulative impact factor: 15.528

Conference paper

1. Krisztina Anita Nagy, Ildikó Y. Tóth, Ákos Kukovecz
Tunable surface wettability of carbon nanotubes-nonwoven textile composites
26th International Symposium on Analytical and Environmental Problems, 23-24 November 2020, Szeged, Hungary, ISBN 978-963-306-771-0

Conferences

Oral presentation

1. Erzsébet Sára Bogya*, <u>Krisztina Anita Nagy</u>, Ákos Kukovecz
Titanate Nanowire/carbon Nanotube Films Evaporation Profile Characteristics
21st International Conference on Chemistry
23-27 September 2015, Csíksomlyó, Romania, ISSN 1843-6293

2. <u>Krisztina Anita Nagy</u>*, Erzsébet Sára Bogya, Ákos Kukovecz, Zoltán Kónya
Water droplet evaporation study from porous carbon nanotube composite films
HSM Annual Meeting
19-21 May 2016, Siófok, Hungary

3. <u>Krisztina Anita Nagy</u>*, Ákos Kukovecz
Comparision of Al_2O_3 and TiO_2 containing elastic nanocomposite hydrogels
12th Conference For Young Scientists in Ceramics
18-21 October 2017, Novi Sad, Serbia

4. Ildikó Y. Tóth*, Erzsébet Sára Bogya, <u>Krisztina Anita Nagy</u>, Attila Egedy, Ákos Kukovecz
Characterization of the solvent specific evaporation from carbon nanotube buckypaperswith different functionalization
22nd International Conference on Graphene, Carbon Nanotubes and Nanostructures,
17-18 September 2018, Berlin, Germany

5. Amit Rawal*, <u>Krisztina Nagy</u>, Krishn Gopal Rajput, Ildikó Y. Tóth, P.V. Kameswara Rao, Sumit Sharma, Akos Kukovecz
Modulating the surface wettability of carbon nanotubes with interface engineering aided three-dimensional (3D) nonwoven material
8th Szeged International Workshop on Advances in Nanoscience
7-10 October 2018, Szeged, Hunagry

6. Krisztina Anita Nagy*, Gergő Ballai, Ágnes Timea Varga, Tamás Varga, Imre Szenti, Judit Kopniczky, Ildikó Y. Tóth, Henrik Haspel, Béla Hopp, Ákos Kukovecz
Oldószerek párolgása egy hidrofób gázdiffúziós rétegen
Műszaki Kémiai Tudományos Bizottság Anyagtudományi-és Szilikátkémiai Munkabizottság, PhD hallgatók anyagtudományi napja
26 November 2018, Veszprém, Hungary

7. Ildikó Y. Tóth*, Krisztina Anita Nagy, Erzsébet Sára Bogya, Gábor Veress, István Sütő and Ákos Kukovecz
Wetting and evaporation properties of carbon nanotube buckypapers doped by hydrophilic nanowires
Chemistry, Physics and Biology of Colloids and Interfaces,
2-6 June 2019, Eger, Hungary

Posters presentation

1. Krisztina Anita Nagy*, Erzsébet Sára Bogya, Zoltán Kónya, Ákos Kukovecz
   Investigation of water droplet evaporation from carbon nanotube and titanate nanowire composite films
   7th Szeged International Workshop on Advances in Nanoscience
   12-15 October 2016, Szeged, Hunagry

2. Krisztina Anita Nagy*, Gergő Ballai, Ágnes Timea Varga, Tamás Varga, Ildikó Y. Tóth, Henrik Haspel, Ákos Kukovecz
   Wetting properties of gas diffusion layers
   HSM Annual Meeting
   24-26 May 2018, Siófok, Hungary

3. Krisztina Anita Nagy*, Gergő Ballai, Ágnes Timea Varga, Tamás Varga, Henrik Haspel, Ildikó Y. Tóth, Ákos Kukovecz
   Wetting and evaporation in the case of Gas Diffusion Layers
   8th Szeged International Workshop on Advances in Nanoscience
   7-10 October 2018, Szeged, Hunagry

4. Krisztina Anita Nagy, Gergő Ballai, Ágnes Timea Varga, Tamás Varga, Imre Szenti, Dániel Sebők, Judit Kopniczky, Ildikó Y. Tóth*, Henrik Haspel, Béla Hopp, Ákos Kukovecz
   Wettability characterization of carbon cloth type gas diffusion layer via infrared thermography and contact angle analysis
   Chemistry, Physics and Biology of Colloids and Interfaces,
   2-6 June 2019, Eger, Hungary

Peer-reviewed papers total: 3 out of this, related to the topic of this thesis: 3

Cumulative impact factor: 15.528 out of this, related to the topic of this thesis:15.528

Independent cites total: 4 out of this, related to the topic of this thesis: 4