

Thesis of the Doctoral (PhD) Dissertation

**Development and Application of NMR Relaxation
Methods for the Structural Characterization of
Carbon Aerogels**

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I. Introduction and Objectives

Ensuring a sustainable energy supply is one of the major scientific and technological challenges of the twenty-first century. With the increasing use of renewable energy sources, there is a growing need for energy-storage technologies capable of compensating for the mismatch between energy production and consumption over time. Batteries and supercapacitors play a key role in this context. In addition to lithium-ion batteries, intensive research is therefore directed towards alternative energy-storage systems, including lithium-sulfur and sodium-ion batteries.

The properties of carbon-based materials used in electrochemical energy-storage systems are strongly determined by their pore structure. The size, volume, distribution and accessibility of micro- and mesopores, together with the high specific surface area, may all be important for the performance of electrode materials. In supercapacitors, a high accessible surface area and an appropriate mesoporous structure are particularly important, whereas in sodium-ion batteries the structure and accessibility of micropores are also relevant.

A wide range of conventional techniques is available for characterizing porous carbon materials, including gas adsorption, electron microscopy and intrusion porosimetry. These methods provide important information on pore size and morphology, but they are not necessarily sufficient on their own to fully describe porous systems in contact with a liquid. The solid-liquid interface formed under operating conditions, liquid penetration into the pores, liquid molecular dynamics and interactions of dissolved ions with the surface introduce additional structural and dynamic parameters.

Aerogels are highly porous, ultralight synthetic materials that can be produced through a sol-gel transition. Carbon aerogels obtained by pyrolysis of organic aerogels may be used, among other applications, as electrode materials and adsorbents because of their high specific surface area and tunable pore structure. The pore structure of resorcinol-formaldehyde-based aerogels can be controlled by varying several synthesis parameters. The final structure depends

on the reactant concentrations, catalyst type and amount, pH, gelation temperature, and the drying and pyrolysis procedures.

The size and aggregation of the primary polymer particles formed during the sol-gel process fundamentally determine the pore structure of the gel. Preservation of the formed pore structure during drying and formation of the carbon framework and microporous structure during pyrolysis are decisive subsequent steps. The composition of the reaction medium and the use of various porogenic or structure-directing components provide further possibilities for structural control. Ionic liquids are particularly interesting in this respect because they can act both as solvents and as structure-directing media during polymerization.

NMR provides several complementary approaches for investigating porous carbon aerogels in the presence of a liquid. NMR relaxometry is sensitive to liquid molecular motion and liquid-surface interactions, NMR cryoporometry can be used to determine pore size and pore-size distributions, whereas NMR diffusometry enables the study of molecular transport within the pore system. Multidimensional relaxation methods provide additional possibilities for distinguishing liquid populations in different dynamic environments.

Interactions between dissolved alkali-metal ions and porous carbon surfaces may be particularly important in electrochemical energy-storage systems. The quadrupolar nature of ^{23}Na makes its relaxation properties sensitive to the local environment. Appropriate NMR methods can therefore be used to identify ion populations in different dynamic states.

The overall aim of my research was to develop and apply NMR-based methods that enable detailed investigation of the structure and liquid-phase behavior of porous carbon aerogels. I compared carbon aerogels prepared by different routes and investigated the structure-modifying effects of the synthesis parameters, the ionic liquid used as a porogen, and graphene oxide as an additive.

The objectives included the liquid-phase characterization of carbon aerogels by NMR relaxometry, cryoporometry and diffusometry, as well as the

investigation of the general applicability of benchtop NMR and the development of new pulse programs. A particular objective was to investigate wetting processes in porous systems by relaxometry and to analyze the effect of polydispersity on the observed behavior.

I also investigated thermal convection occurring in NMR diffusion measurements at elevated temperatures. I aimed to develop a simple experimental procedure for detecting and eliminating this effect.

A further objective was to develop quadrupolar NMR pulse sequences suitable for the investigation of ^7Li , ^{23}Na and related nuclei and for distinguishing ion populations in different dynamic states, including free and bound ions.

II. Methods

A complementary set of methods was used to characterize the structure, pore-size distribution, liquid uptake, liquid-surface interactions and molecular transport processes in carbon aerogels. Low-field NMR formed the central part of the methodology and was complemented by NMR cryoporometry, diffusometry, multiple-quantum NMR measurements and SEM-EDS analysis.

2.1. Preparation of materials

The RF hydrogels were prepared by a base-catalysed polycondensation using a sol-gel process. Three aqueous systems with different polymerization temperatures and catalyst ratios were prepared (RF1-RF3) and denoted CA1-CA3 after carbonization. The graphene-oxide-containing system had a composition similar to RF2; however, GO was added before polymerization at a GO-to-resorcinol mass ratio of 0.02 and the pH was adjusted to 7.

Carbon aerogels synthesized in ionic-liquid/water systems containing 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM-EtSO₄) were used to investigate the effect of the porogenic medium.

After washing and solvent exchange, the gels were converted into aerogels by supercritical drying. Acetone was exchanged for liquid CO₂, and drying was performed at 40-60 °C and 100 bar. The polymer aerogels were carbonized under a nitrogen atmosphere to a final temperature of 800 °C. The heating rate was 5 °C/min, the carbonization time was 1 h, and the nitrogen flow rate was approximately 20 L/min.

2.2. NMR cryoporometry

NMR cryoporometry was used to determine pore size and pore-size distributions. The method is based on the dependence of the freezing and melting temperatures of a liquid confined in pores. Pore size was calculated using the modified Gibbs-Thomson relationship, with water and cyclohexane used as probe liquids.

The freezing and melting curves were fitted with a logistic function. The pore-size density function was obtained from the fitted curve, and differentiation of this function was used to calculate the pore-size distribution.

2.3. Low-field NMR relaxometry

Low-field NMR relaxometry was performed on a Bruker Minispec MQ20 instrument. Longitudinal T_1 relaxation was measured using an inversion-recovery sequence, while transverse T_2 relaxation was measured using a CPMG pulse sequence. In the T_2 experiments, the echo time and number of data points were adjusted to the relaxation range under investigation. The minimum echo time used was 0.08 ms.

To investigate progressive pore filling, water was added to the samples stepwise and relaxometry measurements were performed after equilibration at each stage. Relaxation-time constants were determined by fitting the decay curves with exponential models.

For interpretation of the relaxation data, I used the surface-relaxivity model proposed by Ioan Ardelean, which relates the measured transverse relaxation rate to the ratio of liquid-accessible surface area and pore volume:

$$\frac{1}{T_2} = \xi \frac{S}{V f^k} + \frac{1}{T_{2,bulk}} \quad (1)$$

Where: T_2 : measured relaxation time constant, ξ : surface relaxivity, f : degree of pore filling, S : pore surface area, V : pore volume, $T_{2,bulk}$: relaxation time constant of the bulk liquid.

Using this model, the wetting kinetics and surface hydrophilicity can be estimated from the course of pore filling.

2.4. Two-dimensional T_1 - T_2 relaxometry

T_1 - T_2 correlation relaxometry was also applied to distinguish different liquid populations. In this method, an inversion-recovery period is followed by a CPMG measurement, so that the data contain information on both longitudinal and transverse relaxation. The two-dimensional approach allows liquid populations with different relaxation properties to be separated in the T_1 - T_2

plane and enables comparison of relaxation characteristics related to molecular mobility and surface interactions.

2.5. High-field NMR and NMR diffusometry

High-field NMR measurements were performed on Bruker Avance I 360 MHz and Bruker Avance II 400 MHz instruments. Diffusion measurements were carried out using the pulsed-gradient spin-echo (PGSE) method with the ledbpgp2s sequence and its convection-compensated variant.

Diffusometry was used to study liquid-molecule motion within the pores. The self-diffusion coefficient obtained from diffusion data can be used to investigate geometric restrictions imposed by the pore structure and interactions between the liquid and the pore surface.

2.6. Quadrupolar NMR methods

Multiple-quantum-filtered NMR experiments were applied to investigate motionally restricted sodium-ion populations. In TQF experiments, triple-quantum coherences were generated and reconverted using radiofrequency pulses. To improve sensitivity, a TQTPPI-based approach was also implemented, in which different coherence orders were separated by Fourier transformation, allowing the restricted and free metal-ion populations to be detected simultaneously. A CYCLOPS cycle was incorporated into the readout pulse and receiver phase cycling.

2.7. Scanning electron microscopy

The morphological characterization of the carbon aerogels was complemented by scanning electron microscopy. SEM-EDS measurements were performed at the Institute for Nuclear Research, HUN-REN, using a Bruker electron microscope. The microscope was equipped with an energy-dispersive X-ray detector for determining local elemental composition. The method was particularly useful for characterizing the morphology of graphene-oxide-containing samples.

III. New scientific results of the dissertation

1. I analyzed the NMR relaxometric model previously used to describe pore-wetting mechanisms and established that the model is not suitable for distinguishing uniform and plug-like wetting in highly polydisperse porous systems.

Models used to describe liquid filling of porous materials by NMR relaxometry generally assume a pore system composed of pores with well-defined sizes and shapes, and that the liquid filling the pores can be characterized by a single characteristic transverse relaxation time. In the surface-relaxation model, the T_2 relaxation time of the liquid is related to the surface-to-volume ratio. The model is applicable to well-defined, nearly monodisperse systems, whereas many real porous materials are substantially more complex.

To investigate this problem, I developed a highly polydisperse, well-connected model pore system. The pore system was represented by cylindrical pores whose height was equal to their diameter. I then determined the wetted surface area, liquid volume, the S/V ratio and the corresponding T_2 relaxation time as a function of filling. Two basic filling mechanisms were considered. In uniform wetting, the entire pore surface is progressively wetted while the liquid-layer thickness increases. In plug-like filling, a liquid front advances through the pores from smaller to larger pores, so fully filled and unfilled regions coexist in the system.

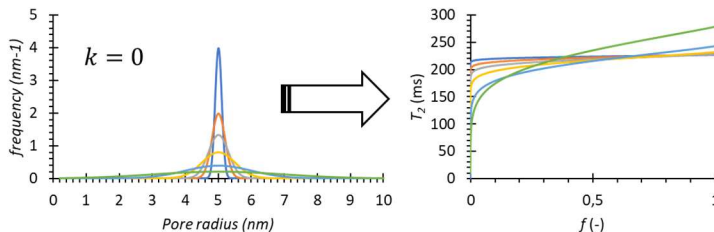


Figure 1. Pore-size distribution of a hydrophobic pore system with a normal pore-size distribution and relaxation curves calculated from the distribution for different standard deviations. For a highly polydisperse pore-size distribution, the calculated relaxometric curves deviate from the model proposed by Ardelean.

The calculations showed that in a highly polydisperse hydrophilic system, uniform filling produces an approximately linear relationship between T_2 and the degree of filling. In a hydrophobic system undergoing plug-like filling, however, a broad pore-size distribution causes the relaxation time to depend on the degree of filling, resulting in a saturation-type $T_2(f)$ curve (Fig. 1).

By explicitly considering the width of the pore-size distribution, I showed that the distribution itself can substantially modify the shape of the filling curve relative to the monodisperse model. This is important for the interpretation of relaxometric wetting curves: a saturation-type curve is not necessarily direct evidence of increased hydrophilicity, but may also arise from polydispersity.

The model calculations refined the interpretation of the liquid-phase investigations of resorcinol-formaldehyde-based carbon aerogels and demonstrated that reliable conclusions require detailed knowledge of the behavior of the model used for interpreting the relaxation data.

2. We developed a simple method for eliminating thermal convection in diffusion measurements performed at temperatures different from the surrounding environment.

We developed a simple method for eliminating thermal convection in diffusion measurements performed at temperatures different from the surrounding environment.

In pulsed-gradient NMR diffusometry, the self-diffusion coefficient of the investigated particles can be determined from signal attenuation. If the sample temperature differs from that of its surroundings, a temperature gradient along the sample axis can generate thermal convection. This coherent flow can cause signal loss similar to that arising from molecular diffusion and can therefore systematically bias the diffusion coefficient.

Sodium alkyl sulfates, namely sodium octyl sulfate (NaOS), sodium decyl sulfate (NaDS) and sodium hexadecyl sulfate (NaHDS), were used to investigate this problem. Measurements were performed at 319 K. These surfactants were particularly suitable because the monomer and micellar mole fractions were known under the experimental conditions, while micelle size could be varied over a broad range by changing the surfactant chain length.

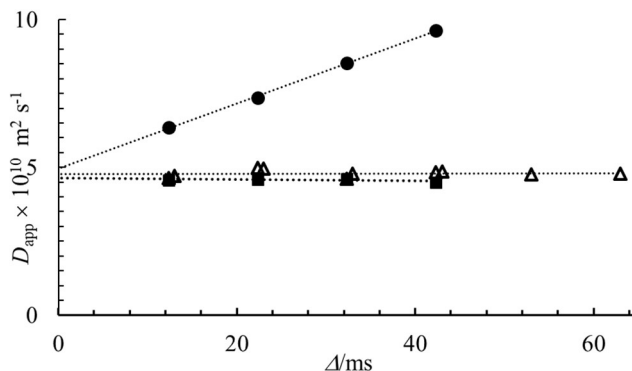


Figure 2. Apparent diffusion coefficient of NaDS micelles as a function of diffusion time at 319 K. Filled circles: 5 mm glass NMR tube, conventional pulse sequence; filled squares: 5 mm sapphire NMR tube, conventional pulse sequence; open triangles: 5 mm glass NMR tube, convection-compensated pulse sequence.

We showed that one of the most important experimental indicators of thermal convection is the dependence of the apparent diffusion coefficient on the diffusion time, Δ . The dependence can be described as:

$$D_{app} \approx D + v^2\Delta \quad (2)$$

where D is the true diffusion coefficient, D_{app} is the measured value, v is the convective flow velocity and Δ is the diffusion time.

The simple correction consists of determining the diffusion coefficient at several diffusion times and linearly extrapolating $D_{app}(\Delta)$ to $\Delta = 0$. The validity of the method was verified using a sapphire NMR tube with high thermal conductivity and measurements performed with a Jerschow-type convection-compensated pulse sequence (Fig. 2).

3. I developed an NMR pulse sequence that allows bound quadrupolar alkali-metal ions (coordinated, mobile within the electrical double layer of a macromolecule, or adsorbed) and free ions to be detected as separate signals and their relative amounts to be determined more accurately than with the previously used sequences.

The relaxation of the quadrupolar ^{23}Na and ^7Li nuclei is sensitive to the local environment and molecular motion. Sodium has a single naturally occurring NMR-active isotope with $I = 3/2$. Under suitable excitation conditions, higher-order coherences can occur. Triple-quantum-filtered relaxation is particularly sensitive to slowly moving sodium ions with long rotational correlation times and has previously been used to detect sodium ions coordinated to biomacromolecules.

As the first step in investigating the interaction between carboxymethylated polyethyleneimine (CM-PEI) and sodium ions, I adapted a TQF (triple-quantum-filtered) pulse sequence that was not available in the instrument pulse-program library. The sequence was implemented from the literature and the six-step phase cycle was extended with a CYCLOPS cycle to reduce phase degradation. The modified TQF sequence was suitable for demonstrating the interaction between sodium ions and CM-PEI.

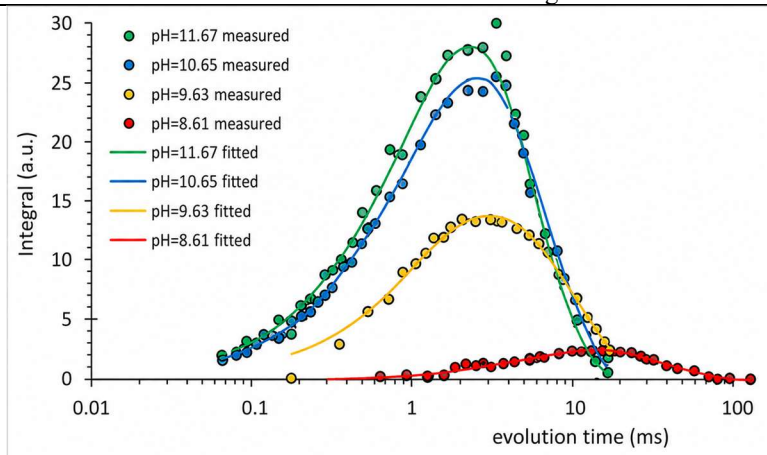


Figure 3. TQF ^{23}Na NMR relaxation curves measured for CM-PEI as a function of the waiting time τ , shown on a semilogarithmic scale. From left to right: pH = 11.67, 10.65, 9.63 and 8.61. $c(\text{CM-PEI}) = 40 \text{ mg/mL}$, $c(\text{Na}^+) = 50 \text{ mM}$.

The TQF relaxation curve can be described by the difference between two exponential components associated with the inner- and outer-sphere relaxation pathways. Because the inner-sphere pathway appears only when ion motion is sufficiently slowed, the method provides a means of distinguishing bound and free forms. In the CM-PEI system, the change in the bound ion population could be followed as a function of pH, demonstrating the relationship between Na^+ binding and the charge state of the macromolecule (Fig. 3).

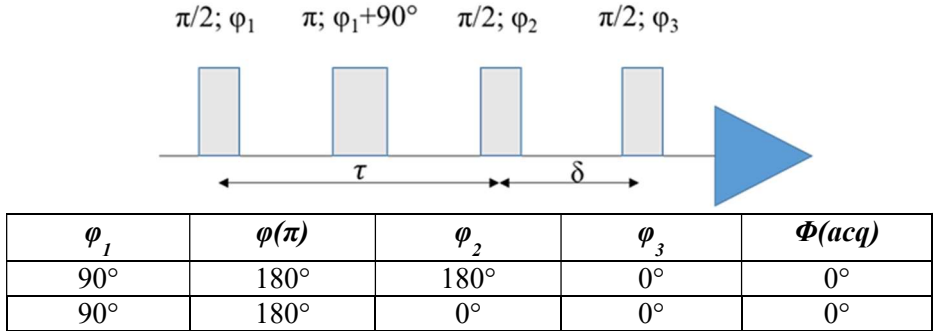


Figure 4. Pulse sequence of the TQTPPI method and the corresponding phase cycle without CYCLOPS phase cycling. Double-quantum filtering is achieved by applying a 180° phase shift to the second 90° pulse.

A major limitation of TQF is signal loss during multiple-quantum filtering, which limits sensitivity. To overcome this limitation, I developed and adapted a TQTPPI (triple-quantum time-proportional phase incrementation) approach. In TQTPPI, different coherence orders are separated by Fourier transformation, avoiding direct filtering and the associated signal loss.

The basic TQTPPI phase program was suitable for short mixing times, but rapid phase degradation occurred at longer mixing times and in heterogeneous systems. I therefore modified the readout-pulse phase and receiver phase using a CYCLOPS cycle and $\Delta p = \pm 2$ coherence selection. This substantially reduced uncertainty arising from phase degradation and enabled more reliable detection of TQ coherence at longer mixing times.

The method was also extended to graphene-oxide suspensions. TQTPPI was used to investigate the state of sodium ions in GO suspensions. Na^+ ions moving within the electrical double layer at the negatively charged GO surface can contribute to the TQ signal; therefore, the method is not restricted to classical coordination complexes.

An important limitation is that the TQ/SQ intensity ratio cannot in general be directly equated with the bound/free concentration ratio if some sodium ions relax during the receiver dead time. This limitation was identified

in the dissertation. Nevertheless, the developed sequence enabled substantially more sensitive and reproducible separation of the bound and free forms.

The modified TQTPPI-based NMR pulse sequence and phase cycle are therefore suitable for the separate detection of bound and free quadrupolar alkali-metal ions and significantly improve signal stability, sensitivity and the reliability of relative-population determination.

4. I developed and applied a 1D and 2D low-field NMR relaxation methodology suitable for determining basic pore-structural and wetting properties of porous systems in a nearly homogeneous magnetic field.

For liquid-phase characterization of carbon aerogels, I developed a complementary set of 1D and 2D low-field NMR relaxation methods and supplemented it with NMR cryoporometry and NMR diffusometry. Low-field relaxometry formed the basis of the methodology. Progressive pore filling was followed by gravimetry and NMR. Since T_2 relaxation is influenced by both liquid-pore-wall interactions and liquid mobility, changes in relaxation time can be used to follow wetting of the pore system.

NMR cryoporometry was used to determine pore shape and pore-size distribution in pore systems filled with water or cyclohexane. The freezing-melting hysteresis can be used to infer pore shape.

NMR diffusometry provided information on liquid mobility in the pores and mass transport between partially filled pores. In partially saturated systems, combined observation of liquid- and vapor-phase transport enabled sequential pore filling to be followed. Different diffusion components also contributed to the distinction between water associated with micropores, surface water clusters, partially filled mesopores and fully saturated pores.

A major extension of the methodology was two-dimensional T_1 - T_2 relaxometry. Each inversion-recovery time point was followed by a CPMG echo train, allowing the data to be evaluated in both longitudinal and transverse relaxation dimensions. In the correlation spectra obtained by two-dimensional Laplace inversion, individual liquid populations can be separated according to their T_1 and T_2 values. The method therefore provides substantially higher

resolving power for complex liquid populations than one-dimensional relaxometry and also improves the robustness of exponential-sum fitting (Fig. 5).

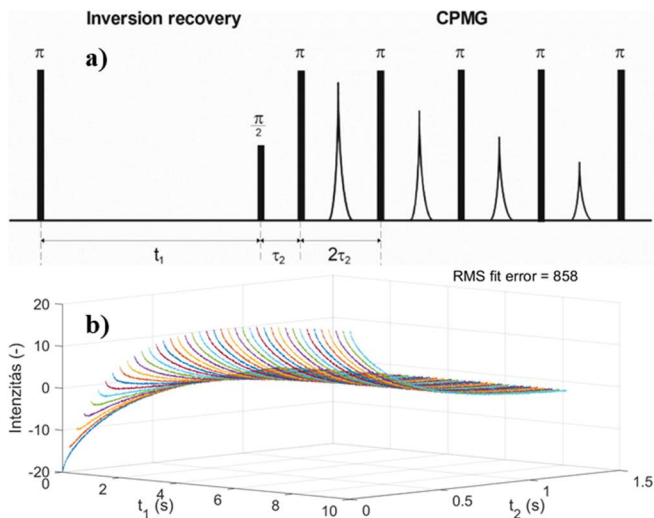


Figure 5. Pulse sequence of the T_1 - T_2 correlation experiment (a) and the primary data set from the T_1 - T_2 correlation experiment on the CA2 carbon aerogel (b). t_1 : longitudinal evolution time; t_2 : transverse evolution time; 2τ : echo time.

I applied the methodology to a graphene-oxide (GO)-modified carbon aerogel. The effect of GO addition on the RF polymer and the resulting carbon aerogel was investigated by SEM, EDS, XPS, N_2 adsorption, cryoporometry and relaxometry. GO incorporation modified the pore structure and surface properties, while interactions between the RF network formed during polymerization and GO persisted in the final carbon structure.

For the graphene-modified carbon aerogel (CAGO), the relaxation results showed substantial differences in the T_2 values of saturated pores compared with the undoped carbon aerogel, together with different filling-dependent wetting behavior. GO incorporation led to a more cylindrical pore shape compared with the spherical RF pores, and this structural change persisted

after pyrolysis. Joint interpretation of cryoporometry and relaxometry indicated the coexistence of hydrophobic and locally hydrophilic surface sites in the GO-modified material.

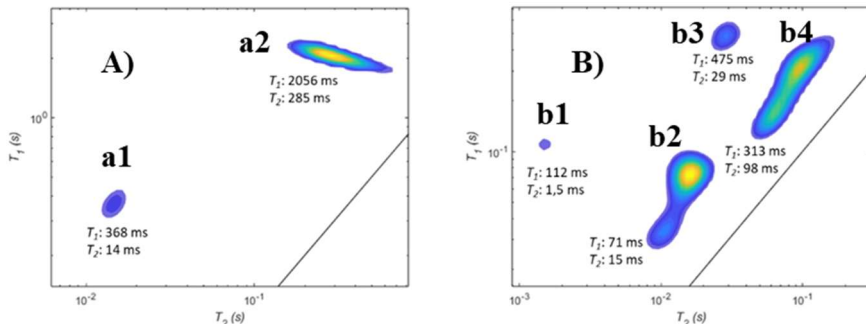


Figure 6. T_1 - T_2 correlation spectra of the partially water-filled pore systems of the CA2 (A) and CAGO (B) carbon aerogels. The different water populations are separated according to their longitudinal (T_1) and transverse (T_2) relaxation times. The black diagonal denotes the $T_1 = T_2$ extreme-narrowing regime associated with weak liquid-surface interactions and rapid molecular motion. Two dominant components are identified for CA2, whereas four distinct water populations are resolved for CAGO.

The T_1 - T_2 correlation experiment also separated liquid populations that could not be clearly resolved in the one-dimensional relaxation spectrum. The two-dimensional spectrum thus enabled comparison of water populations in different states and their interactions with the pore surface (Fig.6).

5. We established that increasing the amount of ionic liquid increases the hydrophilicity of the carbon-aerogel surface while substantially modifying the pore system.

NMR cryoporometry of the CA9, CA30, CA40 and CA50 samples showed that the composition of the ionic-liquid/water mixture strongly affects pore size and pore-size distribution: CA30 and CA40 exhibited well-defined mesoporous structures, whereas CA9 and CA50 were predominantly macroporous.

Relaxometry revealed, in addition to pore-filling water, an additional domain attributable to surface water in samples prepared in the presence of the ionic liquid, indicating modified interactions between water and the carbon surface. The hydrophilicity parameter k was 0.88, 0.58, 0.66 and 0.15 for CA9, CA30, CA40 and CA50, respectively. Relaxometric analysis indicates that at higher ionic-liquid contents the effect is expressed directly in the surface properties, whereas at lower contents the increased water uptake is primarily associated with an increase in micropore volume.

Taken together, the cryoporometric and relaxometric results show that the ionic liquid acts as a porogen not only by tuning pore size and pore-size distribution but also by modifying the surface properties of the carbon aerogel. Increasing ionic-liquid content therefore changes the interaction of the pore system with water and its wettability.

IV. Application potential of the research results

The NMR methods developed during the doctoral research and the qualitative and quantitative information obtained from the carbon-aerogel investigations are primarily applicable to the development and characterization of porous materials. They enable the combined investigation of pore structure, wetting, solid-liquid interfacial interactions and mass transport, and are therefore useful for systems in which the interaction with a liquid phase is as important as porosity itself.

Potential applications of particular importance include porous electrode materials for electrochemical energy-storage systems such as batteries and supercapacitors. The developed methods may contribute to understanding the pore structure, wettability and ion transport of electrode materials and thus to elucidating relationships between structure and operating performance. Quadrupolar alkali-metal NMR methods may also be useful for investigating interactions between ions and solid surfaces.

The methodology may also be applied to adsorbents, catalysts and other functional porous materials in which surface wettability, pore accessibility and liquid transport play important roles. An important advantage of NMR is that porous materials can be investigated while in contact with a liquid.

The developed methods may additionally be extended to broader NMR applications, for example for detecting and correcting errors caused by thermal convection in diffusion measurements.

Publications

I Publications forming the basis of the PhD dissertation:

- (1) Nyul, D.; László, K.; Hollóczki, O.; Kéri, M. Tuning Aerogel Morphology Using Water–Ionic Liquid Binary Mixtures: A Mechanistic Journey from Synthesis to Carbon Properties. *J. Mater. Chem. A* **2026**, 10.1039.D5TA09939K.
<https://doi.org/10.1039/D5TA09939K>.(IF: 9,5, D1)
- (2) Nyul, D.; Kéri, M.; Novák, L.; Szabó, H.; Csík, A.; Bányai, I. NMR Characterization of Graphene Oxide-Doped Carbon Aerogel in a Liquid Environment. *Gels* **2025**, 11 (2), 129.
<https://doi.org/10.3390/gels11020129>.(IF: 7,01, Q1)
- (3) Novák, L.; Miklósi, T. S.; Nyul, D.; Shi, X.; Bányai, I. Synthesis and Characterization of Carboxymethylated Polyethylenimines. *ACS Appl. Polym. Mater.* **2023**, 5 (9), 7208–7219.
<https://doi.org/10.1021/acsapm.3c01090>.(IF: 4,99, Q1)
- (4) Nyul, D.; Novák, L.; Kéri, M.; Bányai, I. A Simple Elimination of the Thermal Convection Effect in NMR Diffusiometry Experiments. *MOLECULES* **2022**, 27 (19).
<https://doi.org/10.3390/molecules27196399>.(IF: 5,27, Q1)
- (5) Kéri, M.; Nyul, D.; Nagyné László, K.; Novák, L.; Bányai, I. Interaction of Resorcinol-Formaldehyde Carbon Aerogels with Water: A Comprehensive NMR Study. *CARBON* **2022**, 189, 57–70. <https://doi.org/10.1016/j.carbon.2021.12.045>.
(IF: 10,39, D1)

II Scientific presentations related to the PhD dissertation

- (1) D. Nyul, M. Kéri, I. Bányai, T. Nagy, Á. Kuki, S. Kéki, L. Nagy: Graphene doped carbon aerogels: Characterization and application, Alpine NMR Workshop, 18-22 September 2025, Bled, Slovenia.
- (2) Dávid Nyul, Mónika Kéri, István Bányai, Sándor Kéki, Lajos Nagy: Preparation and characterization of graphene-containing porous cathodes, XXXI International Chemistry Conference, 2025, Cluj-Napoca, Romania.
- (3) D. Nyul, M. Kéri, I. Bányai, T. Nagy, Á. Kuki, S. Kéki, L. Nagy: Graphene doped carbon aerogels: characterization and application, Alpine NMR Workshop, 20-22 September 2024, Cluj-Napoca, Romania.
- (4) Dávid Nyul, Mónika Kéri, István Bányai, Sándor Kéki, Lajos Nagy: Preparation and characterization of graphene-containing porous cathodes, XXX International Chemistry Conference, 2024, Cluj-Napoca, Romania.

Development and Application of NMR Relaxation Methods for the Structural Characterization of Carbon Aerogels

- (5) D. Nyul, L. Novák, I. Bányai, L. Nagy, S. Kéki: Quadrupolar Relaxation Measurements for Better Understanding of Alkali Metal Ions on Surfaces, Alpine NMR Workshop, 14-17 September 2023, Mátrafüred, Hungary.
- (6) Dávid Nyul, Lajos Nagy, Ákos Kuki, Tibor Nagy, István Bányai, Miklós Zsuga, Sándor Kéki: Application of ⁷Li NMR relaxation methods for the investigation of interfaces in lithium-air batteries, XXIX International Chemistry Conference, 2023, Cluj-Napoca, Romania.
- (7) Dávid Nyul, Levente Novák and István Bányai: Selected applications of ²³Na NMR, NMR Working Group of the Hungarian Academy of Sciences, online autumn scientific session, 2020.
- (8) Dávid Nyul, István Bányai: One-sided NMR, NMR-MoUSE (Mobile Universal Surface Explorer), Szeged, 2019.

III Publications not discussed in the dissertation

- (1) Róth, G.; Nagy, T.; Kuki, Á.; Novák, L.; **Nyul, D.**; Zsuga, M.; Kéki, S. Detailed Compositional and Structure–Property Analysis of Ethylene Oxide-Propylene Oxide Triblock Copolymers. *Macromol. Mater. Eng.* **2025**, *310* (1), 2400297. <https://doi.org/10.1002/mame.202400297>. (IF: 4,91, Q1)
- (2) Nagy, T.; Róth, G.; Kuki, Á.; Pardi-Tóth, V. C.; **Nyul, D.**; Kyzy, Z. K.; Palacios, I. A. I.; Benedek, M.; Nagy, L.; Zsuga, M.; Kéki, S. The Triumvirate of Effective and Rapid Synthesis, Analysis, and Artificial Intelligence to Explore the Structure-Property Relationship of Copolymers. *GIANT* **2024**, *17*. <https://doi.org/10.1016/j.giant.2024.100248>. (IF: 5,38, Q1)
- (3) Nagy, L.; Üneri, H. S.; Kordován, M. Á.; Nagy, T.; Kuki, Á.; **Nyul, D.**; Pál, P.; Erdélyi, Z.; Zsuga, M.; Kéki, S. Organic Solvent-Based Li–Air Batteries with Cotton and Charcoal Cathode. *J. Electrochem. Soc.* **2024**, *171* (4). <https://doi.org/10.1149/1945-7111/ad3857>. (IF: 3,75, Q1)
- (4) Nagy, T.; Kuki, Á.; Róth, G.; Kyzy, Z. K.; Zatalini, A. B.; **Nyul, D.**; Zsuga, M.; Kéki, S. Characterization of Polyacrylamide Diblock Copolymers by Mass Spectrometry Combined with Mass-Remainder Analysis (MARA). *Polym. Test.* **2023**, *117*. <https://doi.org/10.1016/j.polymertesting.2022.107834>. (IF: 5,53, Q1)
- (5) Szabo, L.; Deák, G.; **Nyul, D.**; Kéki, S. Flexible Investment Casting Wax Patterns for 3D-Printing: Their Rheological and Mechanical Characterizations. *POLYMERS* **2022**, *14* (21). <https://doi.org/10.3390/polym14214744>. (IF: 5,37, Q1)
- (6) Udvardy, A.; Szolnoki, C. T.; Kovács, É.; **Nyul, D.**; Gál, G. T.; Papp, G. C.; Joó, F.; Kathó, Á. Water-Soluble Ag(I)-Based Coordination Polymers Obtained by Anion-Directed Self-Assembly of Various AgX Salts and a Phosphobetaine Derived from 1,3,5-Triaza-7-Phosphadamantane. *INORGANICA Chim. ACTA* **2021**, *520*. <https://doi.org/10.1016/j.ica.2021.120299>. (IF: 2,46, Q2)

IV Conference presentations and posters not related to the dissertation

Development and Application of NMR Relaxation Methods for the Structural Characterization of Carbon Aerogels

- (1) M. Kéri, V. Papp, D. Nyul: The role of test liquids in pore morphology characterization, Alpine NMR Workshop, 20-22 September 2024, Cluj-Napoca, Romania.
- (2) M. Kéri, D. Nyul, I. Bánya: Carbon aerogels in NMR tubes, NMR Working Group Meeting, 23-24 May 2024, Balatonszemes, Hungary.
- (3) M. Kéri, D. Nyul, I. Bánya: Carbon aerogels: morphology, surface properties, Alpine NMR Workshop, 14-17 September 2023, Mátrafüred, Hungary.
- (4) M. Kéri, D. Nyul, V. Papp, L. Novák, I. Bánya: A novel way for the characterization of carbon aerogels by NMR relaxation methods, 9th Carbon for Energy Storage and Environmental Protection (CESEP2023), 24-28 September 2023, Budapest, Hungary.
- (5) M. Kéri, D. Nyul, V. Papp, L. Novák, I. Bánya: Characterization of porous materials by NMR relaxation methods, 4th National Chemistry Conference of the Hungarian Chemical Society, 10-12 July 2023, Eger, Hungary.
- (6) Poster: V. Papp, T. P. Kertész, D. Nyul, R. Janovics, I. Bánya, M. Kéri: What can liquid-phase NMR tell us about binders?, 4th National Chemistry Conference of the Hungarian Chemical Society, 10-12 July 2023, Eger, Hungary.
- (7) M. Kéri, D. Nyul, V. Papp, L. Novák, I. Bánya: Application of NMR relaxation methods for aerogels and other porous materials, Workshop on Aerogels Characterization and Modelling, 29-31 March 2023, Debrecen, Hungary.
- (8) Poster: V. Papp, D. Nyul, L. Novák, I. Bánya, M. Kéri: What can liquid-phase NMR tell us about porous materials?, Workshop on Aerogels Characterization and Modelling, 29-31 March 2023, Debrecen, Hungary.
- (9) Poster: D. Nyul, M. Kéri, I. Bánya: The effect of ionic liquid on the morphology and surface properties of RF carbon aerogels by NMR, Workshop on Aerogels Characterization and Modelling, 29-31 March 2023, Debrecen, Hungary.
- (10) M. Kéri, D. Nyul, V. Papp, L. Novák, I. Bánya: Structure and properties of carbon aerogels by NMR, Alpine NMR Workshop, 16-19 September 2021, Bled, Slovenia.
- (11) M. Kéri, D. Nyul, V. Papp, I. Bánya: NMR characterization of porous solids, NMR Working Group Meeting, 13 October 2020, online.
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PhD Publication List

Candidate: Dávid Nyul

Doctoral School: Doctoral School of Chemistry

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List of publications related to the dissertation

Foreign language scientific articles in international journals (5)

1. **Nyul, D.**, László, K., Hollóczki, O., Kéri, M.: Tuning aerogel morphology using water-ionic liquid binary mixtures: a mechanistic journey from synthesis to carbon properties.
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6. Kéri, M., Nagy, Z., Novák, L., **Nyul, D.**, Bányai, I.: A mágneses magrezonancia spektroszkópia (NMR) alkalmazásaa kolloidok fizikai kémiai jellemzésére.
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14. Benedek, M., **Nyul, D.**, Kuki, Á., Fatoye, E. O., Rácz, T., Zsuga, M., Kéki, S., Nagy, T.: Cink-levegő akkumulátorokban alkalmazható hidrogélek előállítása és vizsgálata = Preparation and investigation of hydrogels for use in zinc-air batteries.
In: XXXI. Nemzetközi Vegyészkonferencia = 31th International Conference on Chemistry.
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15. **Nyul, D.**, Kéri, M., Bánai, I., Kéki, S., Nagy, L.: Grafén tartalmú porózus katódok előállítása és jellemzése = Preparation and characterization of graphene-containing porous cathodes.
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17. Nagy, L., **Nyul, D.**, Kuki, Á., Nagy, T., Lakatos, C., Erdélyi, Z., Tócsik, I., Kéki, S.: Termikusan redukált grafén-oxid tartalmú rezorcin-formaldehid széngél katódok tanulmányozása Li-levegő cellákban = Study of resorcinol-formaldehyde carbon gel cathodes containing thermally reduced graphene oxide in Li-air battery cells.
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18. Nagy, T., Kuki, Á., Róth, G., Kordován, M. Á., **Nyul, D.**, Nagy, L., Zsuga, M., Kéki, S.: Zn-levegő akkumulátorok fejlesztése és vizsgálata impedancia spektroszkópiával = Impedance spectroscopy for the development and testing of Zn-air batteries.
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19. Nagy, T., Róth, G., Kuki, Á., Pardi-Tóth, V. C., **Nyul, D.**, Kaldybek, K. Z., Benedek, M., Zsuga, M., Kéki, S.: 4-akriol-morfolin és N-izopropil-akrilamid blokk kopolimerek szerkezet-aggregációs hőmérséklet összefüggésének feltérképezése = Mapping the structure-aggregation temperature relationship of 4-acryloylmorpholine and Nisopropylacrylamide block copolymers.
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20. Kordován, M. Á., Fonó, K., **Nyul, D.**, Zsuga, M., Kéki, S.: Elektromosan vezető kompozitok előállítása és természetként való vizsgálata = Production and testing of electrically conductive composites as a thermistor.
In: XXX. Nemzetközi Vegyészkonferencia = 30th International Conference on Chemistry. Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 67, 2024, (ISSN 2734-7109)
21. **Nyul, D.**, Kéri, M., Bányai, I., Nagy, T., Kuki, Á., Kéki, S., Nagy, L.: Grafén dópolt szén aerogélek előállítása és jellemzése = Synthesis and characterization of carbon aerogels doped with graphene.
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22. Nagy, L., **Nyul, D.**, Kordován, M. Á., Nagy, T., Kuki, Á., Kéki, S.: Grafén-oxid tartalmú szénkatódok alkalmazása Li-levegő akkumulátorokban = Application of carbon cathodes containing graphene oxide in Lithium-air batteries.
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23. Nagy, L., Üneri, H. S., Kordován, M. Á., Nagy, T., Kuki, Á., **Nyul, D.**, Pál, P., Zsuga, M., Kéki, S.: 3D nyomtatással készült Li-levegő cellák tanulmányozása különböző szerves oldószerekkel készült elektrolitok jelenlétében = Study of 3D printed Li-Air battery using electrolyte containing various organic solvents.
In: XXIX. Nemzetközi Vegyészkonferencia = 29th International Conference on Chemistry.
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24. **Nyul, D.**, Nagy, L., Kuki, Á., Nagy, T., Bányai, I., Zsuga, M., Kéki, S.: 7Li-NMR relaxációs módszerek alkalmazása lítium-levegő akkumulátorok határfelületeinek vizsgálatára = Application of 7Li-NMR relaxation methods to study the interfaces of lithium-air batteries. In: XXIX. Nemzetközi Vegyészkonferencia = 29th International Conference on Chemistry. Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 57, 2023, (ISSN 2734-7109)
25. Róth, G., Nagy, T., Kuki, Á., Pardi-Tóth, V. C., **Nyul, D.**, Kaldybek, K. Z., Palacios, I. A. I., Benedek, M., Zsuga, M., Kéki, S.: Kopolimer MALDI-TOF-MS spektrumok elemzése = Analysis of copolymer MALDI-TOF-MS spectra. In: XXIX. Nemzetközi Vegyészkonferencia = 29th International Conference on Chemistry. Ed.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, 59, 2023, (ISSN 2734-7109)
26. Nagy, T., Kuki, Á., Róth, G., Kaldybek, K. Z., Zatalini Balqis, A., **Nyul, D.**, Zsuga, M., Kéki, S.: 4-akriol-morfolin és N-izopropil-akrilamid blokk kopolimerenek előállítása és karakterizálása. In: XXVIII. Nemzetközi Vegyészkonferencia = 28th International Conference on Chemistry. Szerk.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság (EMT), Kolozsvár, 35, 2022, (ISSN 2734-7109)

Foreign language abstracts (2)

27. Benedek, M., Fatoye, E. O., **Nyul, D.**, Kéki, S., Nagy, T.: Synthesis and electrochemical testing of polyacrylic acid based hydrogel electrolyte for Zn-air battery. In: Young Researchers' International Conference on Chemistry and Chemical Engineering: Program and Abstracts, Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, 33, 2025.
28. Róth, G., Kuki, Á., Pardi-Tóth, V. C., **Nyul, D.**, Kaldybek, K. Z., Palacios, I. A. I., Benedek, M., Nagy, L., Zsuga, M., Kéki, S., Nagy, T.: Advanced copolymer analysis by MALDI-TOF MS up to 15 kg/mol. In: ESOPS 24: 22nd European Symposium on Polymer Spectroscopy: Program Book of Abstracts, BAM, Berlin, 48, 2024.

Total IF of journals (all publications): 58,918

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The Candidate's publication data submitted to the Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

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