Ph.D. thesis

Effect of water adsorption on the dielectric properties of materials

Henrik Haspel

Supervisor:
Ákos Kukovecz PhD
Associate professor

Ph. D. School of Chemistry
University of Szeged
Faculty of Science and Informatics
Department of Applied and Environmental Chemistry

Szeged
2014

1. Introduction

The dielectric properties of materials depend strongly on the molecular species adsorbed on their surfaces. The phenomenon is of great scientific and technological importance. In most cases moisture adsorption on hydrophilic materials, and the building up of water layers has to be taken into account. Dielectric processes related to the adsorption play crucial role in the sensing mechanism of some types of sensors, in heterogeneous catalysis, paper-based electronics, industrial processes, hydrophilic food materials and pharmaceutical excipients. Furthermore, the relevance of charge transport processes in macromolecules with biological functions, i.e., carbohydrates, proteins, nucleic acids, cannot be exaggerated.

The understanding of the effect of adsorbate molecules on the dielectric properties of a solid is a prerequisite to the theoretical treatment of the discussed phenomena. Although these processes with utmost scientific and technological importance have been known for more than a century, there is still a lack of their widely accepted, consistent microscopic mechanism.

The main objective of our work was the investigation of water adsorption-related changes in the dielectric properties of hydrophilic materials. We chose hydrothermally synthesized trititanate nanowires (TiONW) as model system, as their physico chemical properties were well known to us. In the past decade, extensive research on the synthesis, characterization and modification of one-dimensional titanate nanowires has been conducted at the Department of Applied and Environmental Chemistry of University of Szeged. Since these nanostructures are hydrophilic ionic oxides with high specific surface area for adsorption and the related dielectric phenomena, i.e., charge carrier generation, ion migration and dielectric relaxation, it provided a great model system for our investigations.

We proposed to study the details of the dielectric changes induced by water adsorption on titanate nanowires. Considerable emphasis have been laid on the characterization of the water content of nanowires, and in particular, on the contribution of different types of water to the measured dielectric response. Moreover, examining the water content and temperature dependence of the dielectric properties, we made an attempt to reveal the molecular origin of the sorption-related changes in the investigated system. We aimed to build a simple theoretical framework, which was able to account for the universal shape of the conductivity characteristics published in the literature for a variety of adsorbent-adsorate pairs in adsorption-induced conduction.

2. Experimental

The titanate nanowire used as model system were synthesized at the Department of Applied and Environmental Chemistry via the alkaline hydrothermal synthesis. Anatase TiO_2 was disperged in NaOH solution until white suspension was obtained. It was further aging in a closed, cylindrical, Teflon-lined autoclave while rotating the whole autoclave intensively around its short axis. Finally, the product was washed with deionised water and HCl acid solution to reach pH = 7 at which point the slurry was filtered and the nanowires were dried in air. During measurements the samples were kept in different constant relative humidity (RH) atmospheres. The humidity in the sample holder was adjusted via various salts in contact with their aqueous solutions.

The size and morphology of the nanowites was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), while elemental analysis was carried out by an energy dispersive x-ray spectrometer (EDS) located in the SEM instrument. The adsorption/desorption isotherms and the specific surface area of the nanowires were characterized by nitrogen adsorption-desorption measurements, while the pore size distribution was calculated from the desorption branch via the Barrett-Joyner-Halenda (BJH) method. The changes in the crystal structure was followed by X-ray diffractometry (XRD). The water content was determined by thermogravimetric analysis (TGA), and the amount of the physisorbed water was quantified by the moisture sorption isotherm, which was calculated from the TGA curves. The state of water on the titanate surface was characterized by Fourier-transform infrared spectroscopy (FT-IR) and low-temperature (-50 °C–25 °C) differential scanning calorimetry (DSC).

Isothermal transient ionic current (ITIC) measurement was employed to reveal the dominant parameters in the changes of electrical conduction during water adsorption. The dielectric properties of titanate nanowires were characterized by dielectric relaxation spectroscopy (DRS) measurements performed in the 10^{-3}-10^{6} Hz frequency range. Dependence of the dielectric processes in the spectra on water content, thermodynamic state of water layers, measuring voltage and temperature were also investigated. The electrical properties were further characterized by the current-voltage (I-V) characteristics of the system.

3. New scientific results

T.1. Charaterization of the type, amount and thermodynamic state of water in titanate nanowires.

1.1. Thermogravimetric analysis revealed that titanate nanowires contain physisorbed, chemisorbed and structural water. XRD measurements showed constant interlamellar distance in nanowires in the 6 - 100% relative humidity range at room temperature, hence only physisorbed water layers contributed to the water dependent electric processes. The moisture sorption isotherm was calculated from the TGA measurements, quantifying the physorbed water content in the system.

1.2. Low-temperature DSC measurements were carried out to characterize the thermodynamic state of the adsorbed water layers. Heating curves above 60 RH% revealed a low-temperature (~-25 °C), while above 90 RH% a further phase transition at higher temperature (~0 °C). The former was assigned to the transition either in the transitional water layers just above the ice-like, strongly bound water molecules or in water layers in the pores of the system. The latter phase transition happened in the liquid-like water layers condensed onto water molecules already bound to the TiONW surface. These layers were in a state similar, but not equal to that of the bulk.

T.2. Analysis of the dielectric response of titanate nanowires; Dependence of the dielectric processes on the amount of adsorbed water.

2.1. Room temperature dielectric spectroscopic and ionic current measurements were carried out in the 6 – 100 RH% range. The electrical conductivity varied exponentially with the relative humidity of the atmosphere. The dependences of the constituent parameters of conductivity, i.e., ionic mobility and charge carrier concentration on humidity were deduced from transient ionic current measurements. The dominant factor in the conductivity changes turned out to be the charge carrier concentration, while ionic mobility had only moderate effect.

2.2. Processes contributing to the damp TiONW dielectric spectra were identified and their origin was critically discussed. There were three relaxations in the medium- and high-frequency regime and a further dispersive feature (low-frequency dispersion, LFD) towards low frequencies. The processes in the low and middle frequency range had interfacial origin, while the high frequency loss arose from the dipolar relaxation of a real polar moiety of the system. The low-frequency dispersion was caused by imperfect charge transport in the sample.

2.3. Dependence of dielectric processes on the amount of adsorbed water was investigated. The conductivity varied exponentially with water content in two separate regions, the latter of which was identified as the third adsorption stage (< 90 RH%) in the moisture sorption isotherm. The relaxation times of the interfacial processes also varied exponentially with the adsorbed amount of water in two separate regions. The change in the shape of the characteristics was again at the beginning of the condensation of the adsorptive molecules.

2.4. A possible correlation between the relaxation times of the low-, and middle frequency range processes and the conductivity was examined. Plotted former quantities against the latter one in the double logarithm formalism resulted in linear curves in two separate regions. On the basis of their similar features these processes were suggested to have a common, interfacial origin.

T.3. Investigation of the temperature dependence of the water-related dielectric response in titanate nanowires.

3.1. The temperature dependence of the processes contributing to the dielectric spectra of nanowires was investigated in the -150 °C - +80 °C range under quasi-isosteric conditions. All investigated processes (interfacial relaxations and conductivity) were temperature activated (followed the Arrhenius-equation) in both, the low (< -20 °C), and the relatively high temperature range (> 0° C).

3.2. The dynamic parameters obtained from the low-temperature measurements could not describe the dielectric behavior of the system above the melting point of water. This implied change in the dynamics of the processes. The common interfacial origin of the middle-frequency peaks implied change in the dynamics of the long range charge transport processes between -20 °C and 0 °C.

3.3. The Arrhenius parameters of the investigated dielectric processes, i.e., activation energy and pre-exponential factor, varied linearly with the amount of adsorbed water. It was pointed out that this behavior is the natural consequence of the interrelation between the water and temperature dependence of these processes.

3.4. Since the pre-exponential factor of every investigated processes (interfacial relaxations, conductivity) varied linearly with the corresponding activaton energies, the compensation effect for conductivity and the middle-frequency losses was demonstrated to be valid in the whole investigated adsorption range.

T.4. Universality in the adsorption-induced conduction processes; a simple theoretical framework.

4.1. A thorough review of the available literature of the last 100 years showed that the dielectric properties of materials with different chemical nature changes during the adsorption of a wide variety of adsorbates according to a characteristics with universal shape. Three separate regions in the conductance characteristics were identified: after an initial mild increase exponential dependence was found, while at the onset of the condensation of the adsorbate a marked change in the characteristics occured. In some cases there was no discontinuity in the characteristics, thus a saturation curve was obtained. The characteristics published for various adsorbent/adsorbate pairs are just parts of a universal sigmoid-like curve.

4.2. In order to understand the universal conductance characteristics a simple theoretical framework was built. The conduction response of the adsorbate molecules provided sigmoid-like characteristics typical in percolation-like behavior, while increasing delocalization of the conduction effect of a single adsorption step gradually transformed the sigmoid curve into the universal characteristics well-known in the literature. The universality of the phenomenon arose from the inherent dynamic and delocalized nature of the charge generation of the adsorption act.

4. Publications related to the present thesis

1. **Water-Induced Charge Transport Processes in Titanate Nanowires: An Electrodynamic and Calorimetric Investigation**
   Haspel H, Laufer N, Bugris V, Ambrus R, Szabó-Révész P, Kukovecz, Á
   The Journal of Physical Chemistry C, 116 (35) 18999–19009 (2012)
   IF(2012): 4.814   cited: -

2. **Water Sorption Induced Dielectric Changes in Titanate Nanowires**
   Haspel H, Bugris V, Kukovecz Á
   The Journal of Physical Chemistry C, 117 (32), 16686–16697 (2013)
   IF(2012): 4.814, cited: -

3. **Water-Induced Changes in the Charge-Transport Dynamics of Titanate Nanowires**
   Haspel H, Bugris V, Kukovecz Á
   Langmuir, 30 (8) 1977-1984 (2014).
   IF(2012): 4.187, cited: -

4. **Dynamic origin of the surface conduction response in adsorption-induced electrical processes**
   Haspel H, Peintler G, Kukovecz Á
   Submitted, (2014)

5. **On a possible universality in conduction processes on solid surfaces**
   Haspel H, Kukovecz Á
   Submitted, (2014)

5. Presentations, posters, attending conferences

1. **Mechanism of humidity sensing: An unfinished story**
   50th anniversary of the first ab initio calculations on organic molecules 1963-2013,
   28-29. October 2013, Szeged, Hungary (oral presentation)

2. **Water sorption-related dielectric changes in titanate nanowires**
   Haspel H, Bugris V, Kukovecz Á, Kónya Z
   7th International Discussion Meeting on Relaxations in Complex Systems (7th IDMRCS),
   21-26. July 2013, Barcelona, Spain (poster presentation)

3. **Identification of water types during the rehydration of a dehydrated CaFe-layered double hydroxide**
   Bugris V, **Haspel H**, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I
   7th International Discussion Meeting on Relaxations in Complex
   Systems (7th IDMRCS), 21-26. July 2013, Barcelona, Spain (poster presentation)

4. **Humidity-sensitive dielectric properties of titanate nanowires (TiONW)**
   Haspel H, Bugris V, Laufer N, Kukovecz Á, Kónya Z
   5th Szeged International Workshop on Advances in Nanoscience (SIWAN5),
   24-27. October 2012, Szeged, Hungary (poster presentation)

5. **A simple and economic way to measure low-temperature quasiisothermal dielectric spectra**
   Haspel H, Bugris V, Király A, Kukovecz Á, Kónya Z
   7th International Conference on Broadband Dielectric Spectroscopy and Its Applications (BDS 2012), 3-7. September 2012, Leipzig, Germany (poster presentation)

6. **Rehydration of dehydrated CaFe-L(ayered)D(ouble)H(ydroxide) followed by dielectric relaxation spectroscopy at low temperature**
   Bugris V, **Haspel H**, Sipiczki M, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I
   7th International Conference on Broadband Dielectric Spectroscopy and Its Applications (BDS 2012), 3-7. September 2012, Leipzig, Germany (poster presentation)

7. **Rehydration of dehydrated CaFe-L(ayered)D(ouble)H(ydroxide)**
Bugris V, **Haspel H**, Sipiczki M, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I
16th International Symposium on Intercalation Compounds (ISIC16),
22-27. May 2011, Sec-Ústupky, The Czech Republic (poster presentation)

8. **Dielectric Spectroscopic Studies on Titanate Nanowires**
6th International Conference on Broadband Dielectric Spectroscopy and Its Applications (BDS 2010), 7-10. September 2010, Madrid, Spain (oral presentation)

9. **Dielectric Spectroscopic Studies on Titanate Nanowires**
The Eights Student Meeting (SM-2009) „Processing and Application of Ceramics", 5. December 2009, Novi Sad, Serbia (oral presentation)

10. 5th International Conference on Broadband Dielectric Spectroscopy and Its Applications (BDS 2008), 26-29. August 2008, Lyon, France

11. **Fluctuation enhanced gas sensing on functionalized carbon nanotube thin films**
Haspel H, Ionescu R, Heszler P, Kukovecz Á, Kónya Z, Gingl Z, Maklin J, Mustonen T, Kordás K, Vajtai R, Ajayan PM
XXII. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2008), 1-8. March 2008, Kirchberg in Tirol, Austria (poster presentation)

12. **Drift effect of fluctuation enhanced gas sensing on carbon nanotube sensors**
Heszler P, Gingl Z, Mingesz R, Csengeri A, **Haspel H**, Kukovecz Á, Kónya Z, Kiricsi I, Ionescu R, Maklin J, Mustonen T, Tóth G, Halonen N, Kordás K, Vahakangas J, Moilanen H
XXII. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2008), 1-8. March 2008, Kirchberg in Tirol, Austria (poster presentation)

13. **Inkjet printed resistive and chemical-FET carbon nanotube gas sensors**
Maklin J, Mustonen T, Halonen N, Tóth G, Kordás K, Vahakangas J, Moilanen H, Kukovecz Á, Kónya Z, **Haspel H**, Gingl Z, Heszler P, Vajtai R, Ajayan PM
XXII. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2008), 1-8. March 2008, Kirchberg in Tirol, Austria (poster presentation)

14. **Low impedance multi-wall carbon nanotube films made suitable for temperature and pressure measurement by localized charge injection**
    Kukovecz A, Smajda R, Őze M, Schaeffer B, **Haspel H**, Kónya Z, Kiricsi I
    XXII. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2008), 1-8. March 2008, Kirchberg in Tirol, Austria (poster presentation)

15. **Buckypaper gas chromatograph: evaporation profile based identification of liquid analytes using multi-wall carbon nanotube films**
    Smajda R, Kukovecz Á, **Haspel H**, Kónya Z, Kiricsi I
    XXI. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2007), 10-17. March 2007, Kirchberg in Tirol, Austria (poster presentation)

16. **On the morphology and transport properties of HDPE–titanate nanowire nanocomposites**
    Szél J, Horváth E, Sápi A, **Haspel H**, Kukovecz Á, Kónya Z, Kiricsi I
    XXI. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2007), 10-17. March 2007, Kirchberg in Tirol, Austria (poster presentation)

17. **Vibrational spectroscopic studies on the formation mechanism of ion-exchangeable titania nanotubes**
    Hodos M, **Haspel H**, Horváth E, Kukovecz A, Kónya Z, Kiricsi I
    XIX. International Winterschool on Electronic Properties of Novel Materials (IWEPNM 2005), 12-19. March 2005, Kirchberg in Tirol, Austria (poster presentation)

6. Other publications

1. **Low-temperature Conversion of Titanate Nanotubes into Nitrogen-doped TiO_2 Nanoparticles**
   Buchholz B, **Haspel H**, Kukovecz A, Kónya Z
   Submitted

2. **Water Types and their Relaxation Behavior in Partially Rehydrated CaFe-Mixed Binary Oxide Obtained from CaFe-Layered Double Hydroxide in the 155 K – 298 K Temperature Range**
   Bugris V, **Haspel H**, Kukovecz Á, Kónya Z, Sipiczki M, Sipos P, Pálinkó I
   Langmuir 29 (43) 13315-13321 (2013)
   IF(2012): 4.187 cited: 1

3. **Rehydration of dehydrated CaFe-L(ayered)D(ouble)H(ydroxide) followed by thermogravimetry, X-ray diffractometry and dielectric relaxation spectroscopy**
   Bugris V, Haspel H, Sipiczki M, Kukovecz Á, Kónya Z, Sipos P, Pálinkó I
   Journal of Molecular Structure 1044 21-26 (2013)
   IF(2012): 1.404 cited: -

4. **Electrical resistivity and thermal properties of compatibilized multi-walled carbon nanotube/polypropylene composites**
   Szentes A, Varga C, Horváth G, Bartha L, Kónya Z, **Haspel H**, Szél J, Kukovecz Á
   Express Polymer Letters 6 (6) 494-502 (2012)
   IF: 2.294 cited: 3

5. **Numerical differentiation methods for the logarithmic derivative technique used in dielectricspectroscopy**
   Haspel H, Kukovecz Á, Kónya Z, Kiricsi I
   Processing and Application of Ceramics 4 (2) 87-93 (2010)
   IF: - cited: -

6. **Carbon nanotube based sensors and fluctuation enhanced sensing**
   Kukovecz Á, M. D., Kordás K, Gingl Z, Moilanen H, Mingesz R, Kónya Z, Mäklin J, Halonen N, Tóth G, **Haspel H**, Heszler P, Mohl M, Sápi A, Roth S, Vajtai R, Ajayan P.M., Pouillon Y, Rubio A, Kiricsi I
   Physica Status Solidi C 7 1217-1221 (2010)
   IF: -   cited: -

7. **Increasing chemical selectivity of carbon nanotube-based sensors by fluctuation-enhanced sensing**
   Molnár D, Heszler P, Mingesz R, Gingl Z, Kukovecz Á, Kónya Z, **Haspel H**, Mohl M, Sápi A, Kiricsi I, Kordás K, Maklin J, Halonen N, Toth G, Moilanen H, Roth S, Vajtai R, Ajayan PM, Pouillon Y, Rubio A
   Fluctuation and Noise Letters 9 (3) 277-287 (2010)
   IF: 0.460 cited: 3

8. **Pyroelectric temperature sensitization of multi-wall carbon nanotube papers**
   Kukovecz Á, Smajda R, Őze M, **Haspel H**, Kónya Z, Kiricsi I
   Carbon 46 (9) 1262-1265 (2008)
   IF: 4.373 cited: 2

9. **Improving the performance of functionalized carbon nanotube thin film sensors by fluctuation enhanced sensing.**
   Kukovecz Á, Heszler P, Kordás K, Roth S, Kónya Z, **Haspel H**, Ionescu R, Sápi A, Maklin J, Mohl M, Gingl Z, Vajtai R, Kiricsi I, Ajayan PM
   Proceedings of SPIE 2008. San Diego, USA, 08.10.2008-08.14.2008 pp. 70370Y/1-70370Y10
   IF: -   cited: -

10. **Fluctuation enhanced gas sensing on functionalized carbon nanotube thin films**
   Haspel H, Ionescu R, Heszler P, Kukovecz Á, Kónya Z, Gingl Z, Maklin J, Mustonen T, Kordás K, Vajtai R, Ajayan PM
   Physica Status Solidi B 245 (10) 2339-2342 (2008)
   IF: 1.166 független hivatkozás: 3

11. **Multiwall carbon nanotube films surface-doped with electroceramics for sensor applications**
Kukovecz Á, Smajda R, Őze M, Schaefer B, **Haspel H**, Kónya Z, Kiricsi I
Physica Status Solidi B 245 (10) 2331-2334 (2008)
IF: 1.166 cited: 5

12. **Drift effect of fluctuation enhanced gas sensing on carbon nanotube sensors**
Heszler P, Gingl Z, Mingesz R, Csengeri A, **Haspel H**, Kukovecz Á, Kónya Z, Kiricsi I, Ionescu R, Maklin J, Mustonen T, Tóth G, Halonen N, Kordás K, Vahakangas J, Moilanen H
Physica Status Solidi B 245 (10) 2343-2346 (2008)
IF: 1.166 cited: -

13. **Inkjet printed resistive and chemical-FET carbon nanotube gas sensors**
Maklin J, Mustonen T, Halonen N, Tóth G, Kordás K, Vahakangas J, Moilanen H, Kukovecz Á, Kónya Z, **Haspel H**, Gingl Z, Heszler P, Vajtai R, Ajayan PM
Physica Status Solidi B 245 (10) 2335-2338 (2008)
IF: 1.166 cited: 4

14. **Temperature response of carbon nanotube films modified with pyroelectric materials**
Smajda R, Kukovecz Á, Őze M, **Haspel H**, Kónya Z, Kiricsi I
Proceedings of the seventh students' meeting – SM-2007 School of Ceramics, 6-8. December 2007, Novi Sad, Serbia and Montenegro, Editors: V.V. Srdic, J. Ranogajec
IF: - cited: -

15. **Vibrational spectroscopic studies on the formation of ion exchangeable titania nanotubes**
Hodos M, **Haspel H**, Horváth E, Kukovecz A, Kónya Z, Kiricsi I
Proceedings of the XIX. Winterschool on Electronic Properties of Novel Materials
AIP Conference Proceedings 786 345-348 (2005)
IF: - cited: 2

16. **Photosensitization of ion-exchangeable titanate nanotubes by CdS nanoparticles**
Hodos M, Horváth E, **Haspel H**, Kukovecz Á, Kónya Z, Kiricsi I
Chemical Physics Letters 399 512-515 (2004)
IF: 2.438 cited: 117

7. Patent

1 Horváth Géza, Szentes Adrienn, Kiricsi Imre, Kónya Zoltán, Kukovecz Ákos, Horváth Endre, Vanyorek László, Haspel Henrik, Szél József
Carbon nanocomposite additive and its use as adjuvant for polymer materials.
WIPO Patent WO/2009/156775 A2 (2009)

Peer-reviewed papers total: 14,	out of this, related to the topic of thesis: 3
Cumulative impact factor: 33.635,	out of this, related to the topic of thesis: 13.815
Independent cites total: 140,	out of this, related to the topic of thesis: -