Thermodynamic Characterization of Nanoscale Materials

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ABSTRACT

"The largest barrier to rational design and controlled synthesis of nanomaterials with predefined properties is the lack of fundamental understanding of thermodynamic and kinetic processes at the nanoscale. …Bulk material properties are not size-dependent, but the properties of nanomaterials are a function of size. The underlying principles governing the properties at all lengths, organization complexity, and structural and property stability over time must be understood to enable the nanoscale materials by design approach."[1]

Quartz crystal microbalance/heat conduction calorimetry, (QCM/HCC) [2] is a new measurement technology that permits high sensitivity measurements in real time of three properties of a nanoscale coating or film undergoing chemical reaction: the mass change (to ±10 nanograms), the heat generated (to ±1 microwatt), and the change in loss compliance of the film. These sensitivities are sufficient to examine the energetics of the formation of a self-assembled monolayer as well as the thermodynamics of the chemical processes in nanoscale polymer coatings. We describe the development of this measurement technology from its beginnings at Lund University and Drexel University to its embodiment in the Masscal G1. We give a number of applications that illustrate its potential to be a key instrumental method of measuring thermodynamic and kinetic processes at the nanoscale.

1 BEGINNINGS OF QCM/HCC

In 1997 I spent a six-month sabbatical leave from the chemistry department at Drexel University in the Department of Thermochemistry of Lund University, hosted by Professor Gerd Olofsson and Professor Ingemar Wadsö. We discussed over coffee one morning the need to measure tiny mass changes in a sample of low volatility inside a heat flow calorimeter. The goal was to determine the enthalpy of sublimation of the material. Heat flow signals from the subliming material were quite high, but the need to remove the sample container and reweigh it on an analytical balance introduced substantial errors in the needed measurement of the mass of material evaporated. I suggested to my hosts that what was needed was to build a small, sensitive balance into the sample chamber itself.

Shortly thereafter, we began work on a sensor that would combine two mature technologies: transverse shear resonators (quartz crystal microbalances) [3] and heat flow sensors and their use in isothermal microcalorimetry [4]. Both have been employed in research laboratories and in commercial instrumentation for many years. Quartz crystal microbalances have been widely used since the 1970's as thickness monitors of thin films deposited in vacuum. Peltier heat flow sensors are the basic sensor in many calorimeters and thermal analysis instrumentation, including those designed and built at Lund University. Our goal was to develop and use a sensor that simultaneously measures the mass change and the heat generated or absorbed when a chemical process occurs on the surface of a bare or coated sensor. The quartz crystal microbalance can measure mass changes at the sub-monolayer coverage because of its nanogram sensitivity. With suitable thermal shielding and temperature control, heat conduction calorimetry can continuously measure sub-microwatt heat flows to or from a reacting sample. If a method could be devised to combine these two technologies in a single sensor, then chemical processes in a thin film sample on the sensor surface could be followed in real time by measuring both the heat and mass changes induced by the chemical or biological process. Since heat and mass are the two fundamental extensive variables needed to determine thermodynamic state variables such as enthalpy, entropy, and Gibbs free energy, we predicted that such a mass/heat flow sensor could be used to determine the thermodynamic quantities associated with the reactions of gases or liquids with thin films.

Here we make a simple estimate of the sensitivity in mass and heat detection needed to detect the energy of binding per unit mass of a monolayer of water on the gold surface of a QCM crystal. The area of the gold electrode exposed to the sample vapor is 2 cm^2. We assume that the monolayer has the density of water itself and a thickness of 0.3 nm, the length of the water molecule. There are thus 2 x 10^{15} water molecules in this monolayer, and their mass is 60 ng. If the binding energy of the water to the gold is taken to be the enthalpy of condensation of water, 44 kJ/mole, then the heat liberated at the surface in forming this monolayer is 0.15 mJ. The mass resolution of the QCM depends on the integration time of the frequency counter used to measure the QCM resonant frequency, but nanogram sensitivity has been widely reported in the literature. Detecting a heat evolution of 150 microjoules in

a heat conduction calorimeter is more challenging, but it has been achieved.

By June of 1997 there was a working mass/heat flow sensor in the Lund laboratory based on the principles described above.

2 DEVELOPMENT OF QCM/HCC

Upon returning to Drexel in the summer of 1997, I worked with graduate student Hamid Shirazi to develop a quartz crystal microbalance/heat conduction calorimeter based on this mass/heat flow sensor. The development, testing, and initial uses of the QCM/HCC are very well documented in Shirazi's Ph.D. thesis, available online [5]. Shirazi performed the following experiments with this new technology:

(A) Solvent vapor sorption into an aliphatic polyurethane film (Tecoflex™) [6]. Solvents employed were ethanol, carbon tetrachloride, chloroform, toluene, acetone, and hexane. The sorption enthalpy and sorption isotherm of each solvent vapor in Tecoflex was determined.
(B) Hydrogen sorption in thin palladium films [2]. Both the sorption isotherm and sorption enthalpy of hydrogen in palladium were measured. The response of the mass/heat flow sensor during the palladium-catalyzed hydrogenation of ethylene was also measured.
(C) Detection of the formation of a self-assembled monolayer of nonylthiol on gold [7]. This experiment was done to test the sensitivity of the apparatus, and it showed that both the mass change and the heat release upon forming a self-assembled monolayer could be detected with the QCM/HCC.
(D) Hydration and dehydration of a thin film of the protein lysozyme[5].

The next graduate student to work on the QCM/HCC was Sister Rose Mulligan, I.H.M.. Her contributions to the development are also described in a Ph. D. thesis available online [8]:

(A) Thermodynamic and rheological properties of Tecoflex upon ethanol vapor and water vapor sorption [9]. Sorption isotherms, sorption enthalpies, and diffusion coefficients of the two gases were determined.
(B) Hydration studies of protein films [10]. Water sorption isotherms, sorption enthalpies and diffusion coefficients were determined in thin films of both lysozyme and myoglobin.

The final Drexel graduate student to work on the QCM/HCC was Jun Tian. His Ph.D. thesis [11] contains the following applications:

(A) Solvent vapor sorption by C_{60} and C_{60}-piperazine films [12]. Solvents used were water, 1,3 dichlorobenzene, carbon tetrachloride, methylene chloride, and benzene.
(B) Water vapor sorption by pharmaceutical film coatings.

All three of these Ph.D. theses contain sections on the theory of operation of each component of the mass/heat flow sensor and experimental details such as block diagrams of the apparatus, sample preparation, data acquisition and control, calibration, and data analysis.

3 BIOLOGICAL APPLICATIONS

Dr. Galit Zilberman joined the research group at Drexel in November 2003. Her previous research at Tel Aviv University with QCM measurements at the solution/electrode interface [13] led us to explore the use of the QCM/HCC as a detector of protein-ligand interactions in aqueous solution [14], and as a detector of the growth of E Coli bacteria on thin film of nutrient medium deposited on the QCM [15].

4 THE MASSCAL G1

In 2001, I founded Masscal Corporation to commercialize the developments we had achieved in the laboratory at Drexel. My goal was to make this technology more widely available to the research community. The first commercial product, the Masscal™ G1, was introduced at the 2004 PITTCON. Its capabilities are well described in company literature, but here are some key specifications:

(A) operating temperature from ambient to 100˚C; temperature stability of ±.005 ˚C without the use of water baths. Ambient operating pressure.
(B) 10 ng sensitivity in mass measurement and 500 nW sensitivity in heat flow measurements with a time constant of 12 seconds (5 datapoints per minute)
(C) Continuous measurement of motional resistance of the coated quartz crystal, a quantity that can be used to determine the loss compliance of the coating[2].
(D) Provisions for the software control of external mass flow controllers to provide a versatile program of gas composition *vs* time in the sample chamber.
(E) Provision for collection of an external analog signal from a detector such as a relative humidity meter.

With funding from the Department of Energy's SBIR program at Masscal, we showed that the G1 could measure both the catalyzed rate of reaction and the

mass build-up or depletion at a platinum or palladium surface when H_2 reacted with C_2H_4 [16].

5 RECENT APPLICATIONS

The following applications of the QCM/HCC technique have been performed with the Masscal G1:

(A) Moisture sorption, transport, and hydrolytic degradation in polylactide films [17]
(B) Monitoring the drying and curing of an alkyd spray enamel [18]
(C) Gravimetric analysis of the non-volatile residue from an evaporated droplet, using the quartz crystal microbalance/heat conduction calorimeter [19]
(D) Moisture sorption and water diffusion coefficients in a multi-layer film of polyethylene oxide and polyacrylic acid (in progress)
(E) Energetics of a self-assembled monolayer of butylthiol on gold (in progress).

6 CONCLUSION

Since many of the materials now being made and characterized in nanotechnology are ultrathin films of thickness < 1 micrometer, their thermodynamic and kinetic properties must be measured with methods more sensitive than the normally employed calorimetric techniques. We believe that the QCM/HCC is ideally suited for such studies, as the references in this article will attest. One key question of importance to nanotechnology is the long-term stability of materials with nanostructures. With atomic compositions varying systematically at the nanometer scale, these nanomaterials contain many more contacts between different functional groups and molecular subunits than do typical materials. How stable are these nanomaterials to moisture, to oxidative degradation? Answers to these questions will determine the ultimate usefulness of the many extraordinary new nanomaterials being synthesized today. Knowledge of the thermodynamics and kinetics of these materials is thus essential in assessing their performance.

REFERENCES

[1] Chemical Industry R&D Roadmap for Nanomaterials by Design, in Chemical Industry Vision 2020 (Solomon, J., ed.) 2003, http://www.chemicalvision2020.org/nanotechnology.html#nano.
[2] A.L. Smith and H.M. Shirazi, Thermochimica Acta 432 202, 2005.
[3] C.-S. Lu and A.W. Czanderna, Applications of Piezoelectric Quartz Crystal Microbalances, Elsevier, New York, 1984.
[4] I. Wadsö, Chemical Society Reviews 1997, 79, 1997.
[5] H.M. Shirazi. Ph. D. thesis, pp. 336, Drexel University, Philadelphia, PA 2000, http://www.library.drexel.edu/er/etheses.
[6] A.L. Smith and H.M. Shirazi, J. of Thermal Analysis and Calorimetry 59 , 171, 2000.
[7] A.L. Smith, S.R. Mulligan, J. Tian, H. Shirazi and J.C. Riggs. in IEEE Frequency Control Symposium, IEEE, Tampa, FL 2003.
[8] S.R. Mulligan. Ph.D thesis, pp. 400, Drexel University, Philadelphia 2003, http://www.library.drexel.edu/er/etheses.
[9] A.L. Smith, S.R. Mulligan and H.M. Shirazi, J. Polymer Sci. Part B Polymer Physics 42 , 3893, 2004.
[10] A.L. Smith, H.M. Shirazi and S.R. Mulligan, Biochimica et Biophysica Acta 1594,150, 2002.
[11] J. Tian., Ph.D. thesis, Drexel University, Philadelphia 2002, http://www.library.drexel.edu/er/etheses.
[12] J. Tian and A.L. Smith. in PV 2002-12 Fullerenes: The Exciting World of Nanocages and Nanotubes (Kamat, P.V., Guldi, D.M. and Kadish, K.M., eds.), Vol. 12, pp. 255, Electrochemical Society, Philadelphia 2002.
[13] L. Daikhin, E. Gileadi, V. Tsionsky, M. Urbakh and G. Zilberman, Electrochimica Acta 45, 3615, 2000.
[14] G. Zilberman and A.L. Smith, Analyst 130, 1483, 2005.
[15] A.L. Smith and G. Zilberman. in 32nd Annual Conference of the North American Thermal Analysis Society (Rich, M., ed.), NATAS - CD-ROM, Williamsburg, VA 2004.
[16] A.L. Smith, H.M. Shirazi and F.C. Smith, Catalysis Letters 104, 199, 2005.
[17] R.A. Cairncross, J.G. Becker, S. Ramaswamy and R. O'Connor. in 27th Symposium on Biotechnology for Fuels and Chemicals Conference, U. S. Department of Energy Biomass Program, Denver, CO 2005.
[18] A.L. Smith. in press (Zarras, P., Richey, B., Wood, T. and Benicewicz, B., eds.) New Developments in Coating Technology, ACS Symposium Series, Washington DC 2006.
[19] A.L. Smith, Journal of the ASTM International in press, 2006.