KPFM investigations on polysiloxane coated gold and glass substrates using pure and functionalized cantilevers

Westfälische Wilhelms-Universität Münster

K. Schmale*, P. Vettikuzha, M. Bernemann, M. Grünebaum, B. Pohl, H.-D. Wiemhöfer

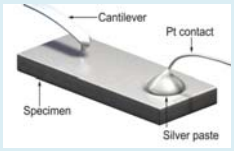
Institute for Inorganic and Analytical Chemistry, Corrensstr. 28-30, 48149 Münster

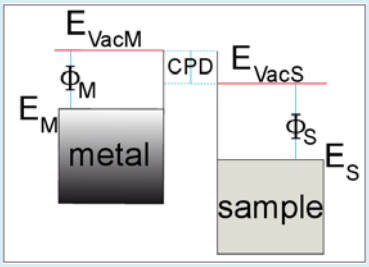
Atomic force microscopy (AFM) measurements provide new insights into the working of battery materials on the micro- and nanoscale. Kelvin Probe Force Microscopy (KPFM) [1] is an AFM mode, where in addition to the sample topography the surface potential of the material can be mapped. On hard substrates this imaging mode can normally be executed quite easily, but sticky samples such as polymers can provide an obstacle.

This can be avoided by using specially functionalized cantilevers, which do not stick to the surface. A model experiment setup was used to gather information on the effect of this functionalization on the measured surface potential, and to determine if KPFM can be a valuable additional method for research on polymer electrolytes or polymer coated electrodes in lithium polymer batteries , e.g. in investigations concerning the ageing of battery materials[2].

KPFM measurements

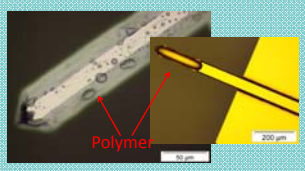
The Kelvin Probe Force Microscopy mode enables measurement of the sample surface potential (SP) and yields information on work function of a surface.





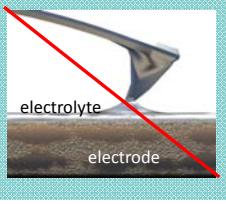
Background

Problem: soft polymer samples contaminate AFM levers and make AFM measurements impossible



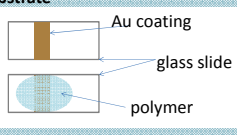
Polymer repellent coating

Aim: avoiding a polymer meniscus during measurements, electrochemical measurements still possible



Samples

Substrate



Preparation:

Preparing glass slides with gold coating by evaporation method

Polymer: mixture of epo-polysiloxane and MEEP-cyclophosphazene (1:1) with DMEDA as crosslinker [3]

Preparing polymer thin films with doctor blade method and crossl-linking at 70 °C

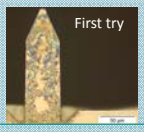
AFM probes

Pure Pt/Ir coated AFM tip
vs.
1-decanthiol functionalized tip

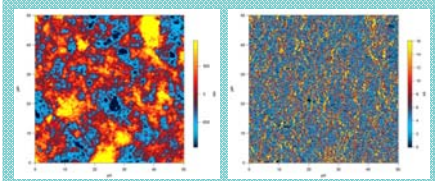
Preparation:

Cleaning of tips by immersing in conc. H_2O_2 for 30 s and then in 0.1 M H_2O_2 + 0.1 M HCl overnight

Coating by immersing in 0.05 mMol decanthiol solution in chloroform over night



Why not take 'real' batteries for comparison?

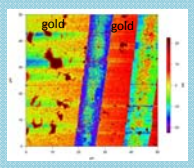


Topography and conductivity image of electrode

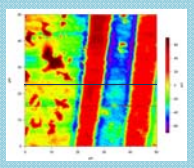
- heterogenous conductivity and surface potential
- relatively high roughness leads to high amount of artefacts in images
- sensitive to humidity and oxygen

Results

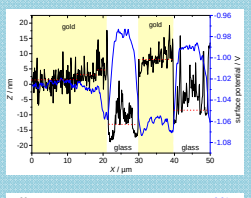
Surface potential difference between glass and gold measured with pure cantilevers

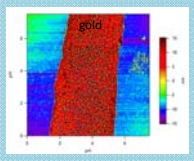


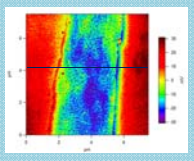
Topography

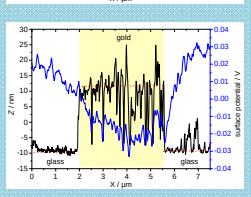


Surface potential



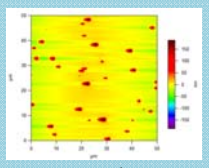




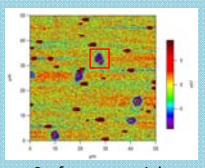


Potential difference between glass and gold is ca. 50 mV. A strong dependence between the SP signal and the gold layer thickness was observed.

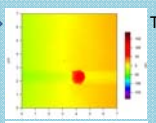
Surface potential difference with polymer coating measured with pure cantilevers



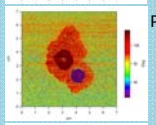
Topography



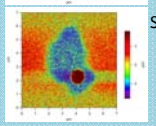
Surface potential



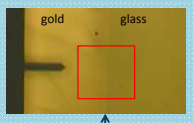
Topo



Phase

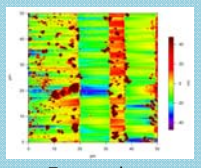


SP

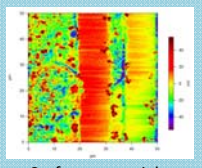


Edge between gold and glass was easily distinguished under the light microscope. A differentiation by the surface potential was not possible, although inhomogenous areas in the polymer (possibly demixing of cyclophosphazene) were found.

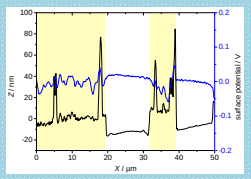
Surface potential difference between glass and gold with functionalized cantilevers (no polymer coating on the sample)



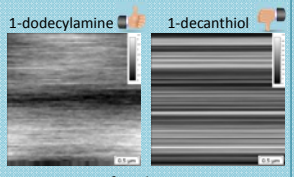
Topography



Surface potential



In an additional test with non-crosslinked polysiloxane on a glass substrate, the qualtity of the topography images was higher if functionalized cantilevers were used. A functionalization with 1-dodecylamine on Si_3N_4 tips showed better results than 1-decanthiol, though, but these tips cannot be applied for KPFM. Therefore, the application of functionalized levers for KPFM imaging of sticky samples is feasible to improve the measurements.



Test of stickyness

Conclusion:

It was shown, that with the KPFM mode it is possible to disthinguish very well between a conductive material and an isolator, and even to measure layer thicknesses of a known material.

Functionalized cantilevers can in priciple be used for KPFM measurements, although in this experimental setup the layer thickness of the polymer was to high to resolve the underlying features even with pure cantilevers. Nevertheless, KPFM can be a usefull tool to improve the knowledge of the processes going on in batteries at the micro- or nanoscale [2].

Literature:

[1] Nonnenmacher et al., *Appl. Phy. Lett.* (1991) **58**: 2921-2923.
[2] Kalinin, Balke, *Adv. Mater.* (2010) **22**: E193-209
[3] Z. Phys. Chemie-Int. J. Res. Phys. Chem. Chem. Phys., **224** (2010) 1439-1473

Acknowledgements:

The authors acknowledge the German Federal Ministry of Education and Research (BMBF) for funding within the collaborative project **KoLiWIn** (03SF0343E) and **AGEF e.V.** for travelling funds.

*Please mail to: kerstin.schmale@wwu.de, phone +49(0)251-8336095