

8. ZUSAMMENFASSUNG

Es wurde die Adsorption der DNA-Basen Thymin, Adenin und Uracil an der Quecksilberelektrode sowie an der Au(111)-Elektrode mittels Zyklovoltammetrie und Chronoamperometrie untersucht, an der Quecksilberelektrode zusätzlich das Verhalten von Mischungen der DNA-Basen.

1. Die theoretisch beschriebenen und am Quecksilber experimentell gefundenen athermischen Cluster konnten erstmalig auch an einer Festkörperelektrode im Experiment nachgewiesen werden. Aus den Ergebnissen kann gefolgert werden, daß ein reiner heterogener Mechanismus der Keimbildung an der Goldeinkristallelektrode (wie er aufgrund der inhomogenen Oberfläche angenommen wird) ausgeschlossen werden kann. Die Existenz athermischer Keime an der Quecksilberelektrode konnte bestätigt werden.

2. Erstmals konnte an der Quecksilberelektrode ein komplettes Set von Stromtransienten gemessen werden, die in ihrer Form theoretisch vorhergesagt waren. Der Oszillationstransient sowie die doppelt invertierte Form des Transienten wurden dabei zum ersten Mal gemessen. Das Auffinden der Transienten bestätigt das Modell der gekoppelten Prozesse von Adsorption, Nukleation und Keimwachstum. Ein überwiegend direkter Einbau der Moleküle aus der Lösung in die kondensierte Phase (direct impingement) ist mit diesem Modell und den gefundenen Transienten nicht zu erklären, und findet daher wahrscheinlich nicht statt. Aus dem gemessenen Oszillationstransienten folgt ebenfalls, daß die Adsorption an die Elektrode nicht diffusionskontrolliert, sondern eher aktivierungskontrolliert ist.

3. Der Einfluß des Elektrolytwiderstands auf die verschiedenen Transientenformen wurde über die Variation der Zellkonstanten RC durch einen vorgeschal-

teten Widerstand untersucht. Die Form der Transienten wird dabei stark vom unkompensierten Widerstand beeinflusst. Eine Abschätzung des unkompensierten Widerstands im Experiment ist unerlässlich für eine Einschätzung, ob der zu untersuchende Prozeß unter potentiostatischen oder nichtpotentiostatischen Bedingungen abläuft.

4. Ergebnisse, die am Quecksilber gewonnen wurden, sind nicht ohne weiteres auf die Goldeinkristallelektrode übertragbar. Wahrscheinlich führt eine zusätzliche Faradayreaktion an der Goldelektrode dazu, daß das Modell der drei gekoppelten Prozesse Doppelschichtumladung, Adsorption und Kondensation, die rein kapazitiver Natur sind, in diesem Fall nicht anwendbar ist.

5. Es wurde gezeigt, daß die Methode der invertierten Stromtransienten angewendet werden kann, um das Potential maximaler Adsorption E_m und das Nullladungspotential PZC für verschiedene Adsorptionszustände auf eine einfache Art und Weise zu bestimmen. Mit Hilfe dieser Methode wurde im System Thymin/Quecksilber eine Reorientierung der Moleküle während des Phasenübergangs festgestellt. Aus der Verschiebung des PZC zu positiveren Potentialen gegenüber dem Leitelektrolyten und der Position des E_m kann auf eine Orientierung geschlossen werden, in der Thymin in der kondensierten Phase planar und in der nichtkondensierten Phase etwas gekippt, mit dem negativen Ende des Dipols an der Grenzfläche, angeordnet ist. Auf keinen Fall sind die Moleküle in der kondensierten Phase senkrecht orientiert.

6. Die Zusammensetzung des kondensierten Thyminfilmes hängt vom Startpotential ab. Bei anodischen Potentialen kommt es an der Elektrode zur Koadsorption von neutralen Thyminmolekülen und Thyminanionen. Die Anionen nehmen nicht an der Bildung des kondensierten Filmes teil, werden jedoch teilweise mit eingebaut.

7. Je näher die Meßtemperatur bei der Kondensationstemperatur liegt, desto weniger kommt es zur Reorientierung der Moleküle. Dieser Temperatureffekt liegt im geringer werdenden Dichteunterschied der beiden beteiligten Phasen begründet, der definitionsgemäß bei der Kondensationstemperatur Null wird.

8. Im System Adenin/Quecksilber kommt es ebenfalls zu einer Reorientierung der Moleküle während des Phasenübergangs. Der PZC wird allerdings gegenüber dem Leitelektrolyten zu negativeren Potentialen verschoben. Es läßt sich eine wahrscheinliche Orientierung ableiten, bei der die Moleküle in der nicht-kondensierten Phase leicht angekippt, mit dem negativen Ende des Dipols zur Elektrode angeordnet sind und sich beim Übergang in die kondensierte Phase weiter aufrichten.

9. In einer Mischung der beiden Komplementärbasen Thymin und Adenin bildet nur die im Überschuß vorhandene Base einen kondensierten Film an der Grenzfläche. Dieser wird durch die jeweilige komplementäre Base erheblich gestört. Die jeweilige komplementäre Base nimmt nicht an der Filmbildung teil, sondern destabilisiert im Gegensatz dazu den kondensierten Film. Eine 1:1 Mischung der beiden DNA-Basen bildet keinen kondensierten Film mehr. Es kommt hier zwar zur Koadsorption, aber die lateralen Wechselwirkungen zwischen Thymin und Adenin sind nicht stark genug, um eine gemischte Phase mit höherer Dichte zu bilden. Dieser Effekt kann durch eine unterschiedliche Orientierung der Moleküle an der Elektrode erklärt werden, die stärkere attraktive Wechselwirkungen (wie z. B. Wasserstoffbrücken) nicht zuläßt.

10. Im System Uracil/Quecksilber konnte unter den experimentellen Bedingungen keine Reorientierung der Moleküle während des Phasenübergangs beobachtet werden. Uracil ist an der Quecksilberoberfläche ähnlich orientiert wie Thymin.

11. Zwischen den beiden nichtkomplementären Basen Thymin und Uracil besteht an der Grenzfläche keine vergleichbar starke attraktive Wechselwirkung wie zwischen den jeweils reinen Substanzen. Die jeweilige Base im Unterschuß bleibt an der Grenzfläche adsorbiert. Sie führt nicht zu einer solch starken Destabilisierung des kondensierten Films wie bei den komplementären Basen. In einer 1:1 Mischung (entsprechend der Grenzflächenkonzentration) findet bei tiefer Temperatur ein Phasenübergang statt. Es wird allerdings keine gemischte kondensierte Phase gebildet. Dabei kann nicht entschieden werden, ob die kondensierte Phase

in den Mischungen der beiden Basen nur aus einer Substanz besteht, oder ob Domänen von beiden Basen vorliegen.

9. SUMMARY

The adsorption of the DNA-bases thymine, adenine und uracil was studied at the mercury and the Au(111) electrode by cyclic voltammetry and chronoamperometry. The behaviour of mixtures of these bases was studied at the mercury electrode.

1. Theoretically known and until now only found at the mercury electrode, the existence of athermal clusters was experimentally proved for the first time at a solid electrode. It can be concluded from the results that a pure heterogeneous mechanism of nucleation (as it is assumed because of the inhomogeneous surface) can be excluded at the gold single crystal surface. The existence of athermal clusters at the mercury electrode could be confirmed.
2. For the first time a complete set of current transients, the shape of which was already theoretically predicted, could be measured at the mercury electrode. The oscillation transient as well as the doubly inverted shape of the transient have not been measured before. The finding of these transients confirms the model of the coupled processes of adsorption, nucleation and growth. A predominantly direct impingement of the molecules from the solution into the condensed phase is not explainable with this model, and does therefore probably not take place. It follows also from the measured oscillation transient that the adsorption at the electrode is not diffusion controlled, but rather activation controlled.
3. The influence of the electrolyte resistance on the different shapes of transients was examined by the variation of the cell constant RC by an additional external resistor. The shape of the transients is strongly influenced by the uncompensated resistance. An estimation of the uncompensated resistance in the experiment is

therefore essential for the decision whether the examined process runs under potentiostatic or non-potentiostatic conditions.

4. Results from the mercury electrode cannot simply be transferred to the gold single crystal surface. Probably an additional faradaic reaction at the gold electrode is the reason why the model of the three coupled processes adsorption, condensation and charging of the electrochemical double layer (which are all of pure capacitive nature) cannot be applied in this case.

5. It was shown that the method of the inverted current transients can be applied to determine the potential of maximum adsorption E_m and the potential of zero charge PZC for the different adsorption states in an easy way. A reorientation of the molecules during the phase transition in the system thymine/mercury was found by this method. From the shift of the PZC to a positive potential compared with the supporting electrolyte in combination with the position of E_m an orientation of thymine can be concluded in which the molecules in the condensed phase are arranged planar and in the non-condensed phase slightly upright with its negative ends to the surface. By no means the molecules in the condensed phase are oriented perpendicularly.

6. The composition of the condensed thymine film depends on the startpotential. Coadsorption of neutral thymine molecules and thymine anions occurs at anodic potentials. The anions do not take part in the formation of the condensed layer, but are nevertheless partly present in the condensed phase.

7. The more the temperature of the measurement approaches the condensation temperature, the smaller becomes the reorientation of the molecules. The reason for this temperature effect lies in the shrinking difference of the density between both phases, which becomes zero by definition at the condensation temperature.

8. There occurs also a reorientation of the molecules during the phase transition in the system adenin/mercury. The PZC is shifted to a more negative potential compared to the supporting electrolyte. A probable orientation can be concluded, in which the molecules in the non-condensed phase are arranged slightly

upright with its negative ends to the electrode, and change to a more upright position in the condensed phase.

9. Only the respective base in excess concentration forms a condensed layer at the interface in a mixture of both complementary bases thymine and adenine. The formation of this condensed layer is considerably disturbed by the respective complementary base. The complementary base does not take part in the film formation, on the contrary, it destabilizes the condensed film. No condensed layer is formed in a 1:1 mixture of the bases. Though the bases coadsorb, the lateral interactions between thymine and adenine are not strong enough to form a mixed phase of higher density. This can be explained by a different orientation of both kinds of molecules at the electrode, which prevents stronger attractive interactions between them (like by hydrogen bridges).

10. No reorientation during the phase transition could be observed in the system uracil/mercury under the experimental conditions. Uracil is adsorbed at the mercury surface in a similar way as thymine.

11. There is no attractive interaction between the non-complementary bases thymine and uracil at the interface, which is of comparable strength like between the pure substances. The respective base in the minor concentration remains adsorbed at the interface. It does not cause such strong destabilization of the condensed film like in the case of the complementary bases. A phase transition occurs in the 1:1 mixture (regarding the surface concentration) at low temperature, but a mixed condensed phase is not formed. It cannot be decided whether the condensed phase of the mixtures is composed of only one substance, or domains of both bases exist.

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SYMBOLE

CE	Gegenelektrode (counter electrode)
CV	Zyklovoltammetrie (cyclic voltammetry)
DL	Doppelschicht (double layer)
PZC	Nullladungspotential (potential of zero charge)
R	Ohmscher Widerstand
RE	Bezugsselektrode (reference electrode)
SCE	gesättigte Kalomelektrode (saturated calomel electrode)
SNIFTIRS	(subtractively normalized interfacial fourier transform infrared spectroscopy)
STM	Rastertunnelmikroskopie (scanning tunneling microscopy)
WE	Arbeitselektrode (working electrode)
c	Konzentration organischer Filmbildner in der Lösung (Bulkkonz.)
C	Kapazität
E	Potential
E_{act}	Ist-Potential, Potential, das aktuell an der Arbeitselektrode anliegt
E_{soll}	Soll-Potential der Arbeitselektrode
E_i	Präpolarisationspotential, Startpotential (initial potential)
E_f	Sprungpotential (final potential)
E_{cp}	Schnittpunkt der Ladungs-Potential-Kurven von adsorbierter und kondensierter Phase (crossing point potential)
E_m	Potential der maximalen Adsorption, ohne Reorientierung
E'_m	Potential der maximalen Adsorption der kondensierten Phase, mit Reorientierung während der Kondensation
E_{PZC}^0	Nullladungspotential des reinen Leitelektrolyten
E_N	Verschiebung des PZC bei komplett mit Adsorbat bedeckter Grenzfläche, ohne Reorientierung
E'_N	Verschiebung des PZC bei komplett mit Adsorbat bedeckter Grenzfläche, mit Reorientierung während der Kondensation

i_{ads}	Strom, der durch die Adsorption hervorgerufen wird
i_{dl}	Strom, der durch die Doppelschichtumladung hervorgerufen wird
i_{re}	Strom, der durch die Reorientierung hervorgerufen wird
q_0	Ladungsdichte für $\Theta = 0$
q_1	Ladungsdichte für $\Theta = 1$
t	Zeit
t'	Abbruchzeit der Keimbildung
t_{ind}	Induktionszeit
ΔG^0	freie Standardadsorptionsenthalpie
Θ	Bedeckungsgrad
Θ_{ext}	Bedeckungsgrad ohne Überlappung der wachsenden Zentren

Veröffentlichungen

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- C. Donner, St. Kirste, L. Pohlmann, H. Baumgärtel; Chem. Phys. Lett. 280 (1997) 287-295 The appearance of athermal nuclei of thymine at Au(111) and the shape of current-time transients
- C. Donner, St. Kirste, L. Pohlmann, H. Baumgärtel; Langmuir 14 (1998) 6999-7007 Inverted current-time transients. A new method for the determination of the potential of maximum adsorption in condensed layers
- C. Donner, L. Pohlmann, St. Kirste, H. Baumgärtel; Chem. Anal. 45 (2000) 175-188 Two-dimensional condensation of small organic molecules at electrodes
- C. Donner, St. Kirste; Langmuir 17 (2001) 1630-1636 Influence of the electrolyte resistance on the transient response in nonfaradaic phase transition experiments on mercury and Au(111)
- S. Kirste, C. Donner; PCCP 3 (2001) 4384-4389 Coadsorption of the complementary base pair adenine-thymine at the mercury/electrolyte interface

Poster:

- 7th International Fischer Symposium on „Scales in electrochemical systems - from Ångströms to meters“ Karlsruhe 15.-19. Juni 1997 „The physical meaning of current-time transients“ C. Donner, L. Pohlmann, S. Kirste, H. Baumgärtel
- Bunsentagung 1998 Münster 21.-24. Mai 1998 „Inverted current-time transients - a new method for the determination of the potential of maximum adsorption in condensed layers“ S. Kirste, P. Stöckel, C. Donner, H. Baumgärtel
- Conference on electrified interfaces: Dynamics, structure and chemical modifications at electrified interfaces Portucalensis, Portugal 5.-10. Juli 1998 „Inverted current-time transients – A new method for the determination of the potential of maximum adsorption in phase transition experiments“ C. Donner, L. Pohlmann, St. Kirste, H. Baumgärtel
- GEI-98 Luigi Galvani Anniversary Meeting 23.-26. September 1998 Bologna, Italien „Determination of the potential of maximum adsorption in two-dimensional condensed adsorbate layers - a study of the system thymine/mercury“ C. Donner, L. Pohlmann, St. Kirste, H. Baumgärtel
- Euroconference on modern trends in electrochemistry of molecular interfaces Majvik, Kirkkonummi, Finnland, 28.8.-3.9.1999 „Coadsorption in condensed layers“ S. Kirste, C. Donner
- International conference on electrified Interfaces Wolfville, Nova Scotia, Canada, 9.-13. Juli 2001 „Chronoamperometric studies of organic monolayers on mercury and Au (111)“ C. Donner, St. Kirste

Vortrag: Bunsentagung 1999 Dortmund 13.-15. Mai 1999 „Koadsorption in kondensierten Schichten“ C. Donner, S. Kirste

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