CDFA: Molecular electronics and hybrid structures

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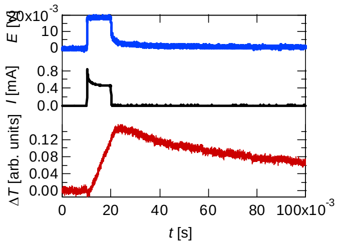
Redox Reactions at Electrode Surfaces

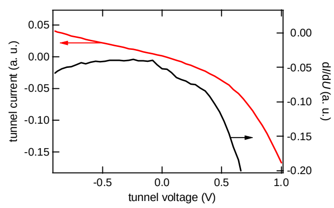
sovent effects / hydration

-microcalorimetry of electrochemical redox reactions



‚electronic structure' and electron transfer

-tunneling spectroscopy under ambient and electrochemical conditions



-Microcalorimetry of electrochemical reactions

In *electrochemical* calorimetry:

electrical work: $w_{el,m} = z \cdot F \cdot \phi = -\Delta_R G = -(\Delta_R H - T\Delta_R S);$

from the ‚chemical reaction'

heat transfer from surrounding

$$\Rightarrow \boxed{q_m = \Delta_R G - \Delta_R H = -T\Delta_R S;}$$ Ostwald (1903)

What for? $\Delta_R S$ contains stoechiometry of the reaction!

main contributions for redox reactions like $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$:
- -*entropy of solvation*, i.e., reorganization of the hydration shell
- -in addition, particularly for anchored redox centers entropy, due to *coadsorption of anions and cations*

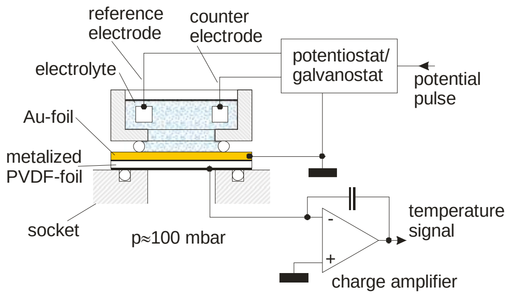
But: ‚monolayer sensitivity' is required!

Can we achieve „monolayer sensitivity“?

Use thin electrode/sensor assembly with *low heat capacity*

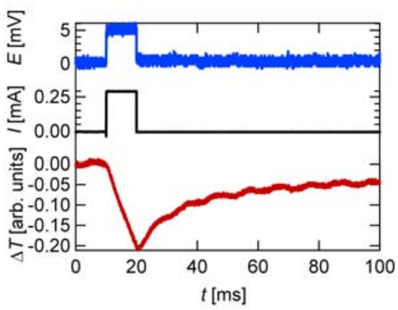
Use pulsed electrochemical reactions:

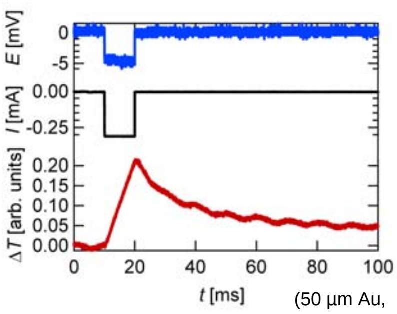
- -fast enough to *avoid heat loss into the electrolyte (and uptake of Joule heat from the electrolyte)*
- -slow enough to ensure *thermal equilibration of the electrode/sensor assembly*



C. E. Borroni-Bird, and D. A. King, Rev. Sci. Instr. **62** (1991) 2177.
J. T. Stuckless, N. A. Frei, and C. T. Campbell, Rev. Sci. Instr. **69** (1998) 2427.

Oxidation /reduction of 0.06 monolayer of $Fe(CN)_6^{3-/4-}$





(50 µm Au, 0.1 M $[Fe(CN)_6]^{3-/4-}$)

oxidation:
$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$

$\Delta T < 0 \Rightarrow \Delta S > 0$

release of water from hydration shell

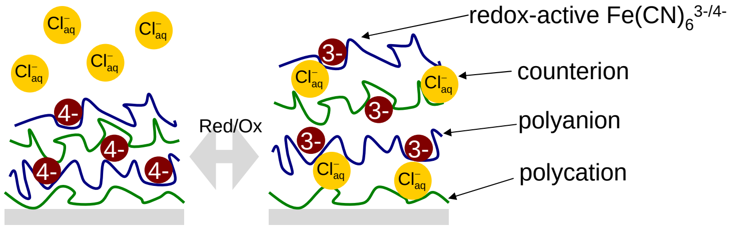
reduction:
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$

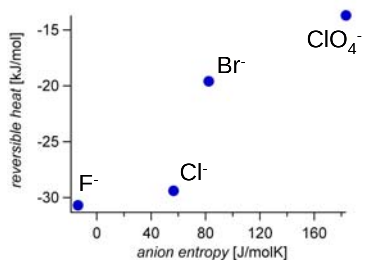
$\Delta T > 0 \Rightarrow \Delta S < 0$

bonding of water in hydration shell

$\Delta S \approx 45$ J/molK

Swelling/deswelling of electroactive polyelectrolyte-multilayers: Role of entropy for the stabilization of the multilayers?

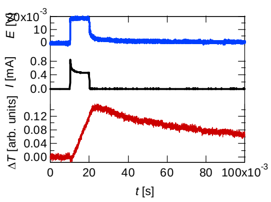




Ferrocyanide in PEM (50 µm Au-foil, in 100 mM X^- (pH 7,4)

K. Bickel (KIT), R. Zahn(ETH) and T. Zambelli (ETH)

Objectives:

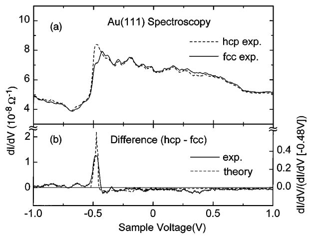


Microcalorimetry:
entropic contribution (hydration shell, counter ions etc.) to $\Delta_R G$ of the charge transfer

study ‚anchored‘ redox molecules:
- ferrocene modified thiols on Au
- viologenes
- metalloporphyrins, etc.

Scanning Tunneling Spectroscopy (STS) in Electrochemical Environment

STS is well established in UHV, preferentially at low temperature



Au surface state at -0.5 V at 4 K in UHV

Chen et al., PRL 80,1469 (1998)

STS in electrochemical environment !?

-LDOS

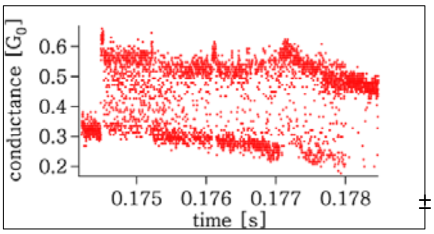
-mechanism of charge transfer surface→molecule→tip

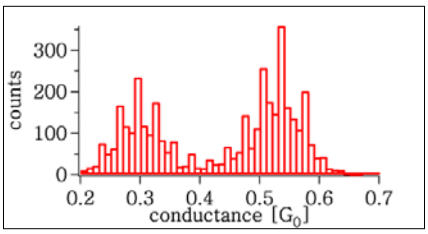
only very few experiments: Tao, Simeone and Kolb, Wandlowski et al.

Problems with Electrochemical STS

- stability of the tunneling gap, i.e., two level fluctuations

  Au(111) / Au-tip in air, U_T = 10 mV

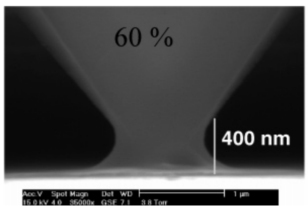




meniscus formation in humid air

we observed fluctuations up to 20 MHz

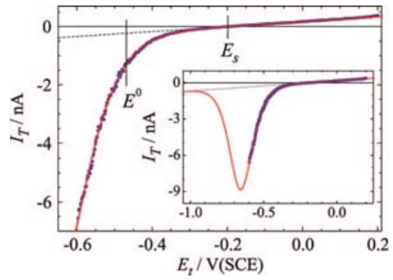
fluctuations were also observed in vacuum
(e.g., R. Hoffmann et al., Nanotechn. **18**, 395503 (2007)),
but to much less extent, mostly upon atomic contact



Weeks et al., Langmuir 21, 8096 (2005)

Problems with Electrochemical STS (cont.)

-electrochemical reactions at tip and sample limit the applicable U_{sample} and U_{tip}



viologene/Au(111)

Pobelov, Li, and Wandlowski, JACS **130**, 16045 (2008)

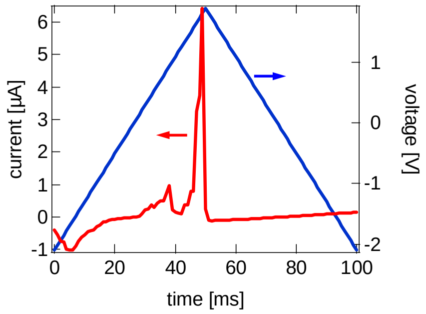
often: variation of U_{sample} at fixed $U_{bias} = U_{tip} - U_{sample}$

$\Rightarrow$ change of the electrochemical condition

-mechanical stablitity of most EC STMs

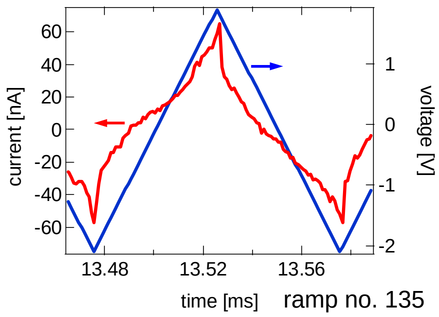
Our approach: -fast ramps

Au in air
slow voltage ramp (±2V, 100ms)



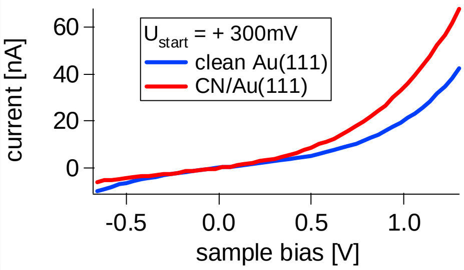
unstable gap,
due to electrochemical
water decomposition

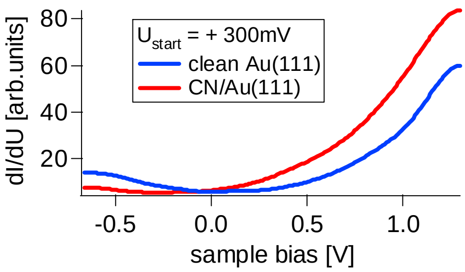
repetitive, fast voltage ramps (±2V, 100µs)



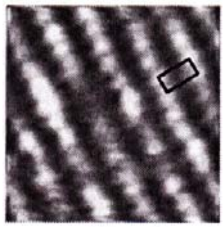
ramp no. 135

stable gap
for up to 1000 ramps (=100ms)





CN/Au(111) (1.15x√3R30°)

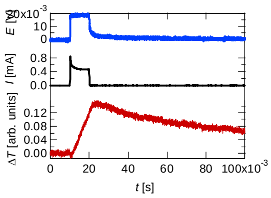


($3.3x3.3nm^2$)
Yamada, JCP **113**, 1217 (2000)

-no Au surface state on clean Au(111) in humid air

-strong asymmetry of I(U) for CN/Au(111)

Objectives:



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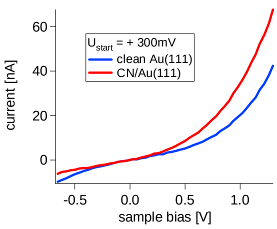

STS:
-relyable measurements under EC conditions
-study ‚anchored‘ redox molecules
-redox reaction rates