Redox active layer-by-layer self-assembled polyelectrolyte thin films

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Layer-by-layer Self-Assembly



G. Decher. Science 277, 1232 (1997).

Synthesis of Layered Polyelectrolyte Membranes is a Simple "Dip n' Rinse" Procedure



Polyelectrolyte Building Blocks





Joseph B. Schlenoff www.chem.fsu.edu/multilayers



Charged substrate and assembly of first polyelectrolyte monolayer



Charged substrate, first monolayer and assembly of second polyelectrolyte monolayer



Charged substrate, first bilayer and assembly of third polyelectrolyte monolayer



Fig. 2. Scheme of the electrostatic layer-by-layer self-assembly (ESA)



Interpenetration of polyelectrolyte layers has been demonstrated by neutron reflectivity (G. Decher, Science 277, 1232 (1997).

Combination of LB and LbL Self-Assembly





Figure 5. Schematic of the preparation of hetero-superlattices (-mixed layers of lipids and polyelectrolytes) by transfer of the floating multilayers onto hydrophobized solid substrates with the Langmuir-Blodgett technique.

G. Decher et. al., Langmuir 2000, 16, 8871-8878

Structure





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Electrochemical Quartz Crystal

Microbalance (EQCM)









E.J. Calvo, E. Forzani, M. Otero, J. Electroanal. Chem., 538/539, 2002, 231-241.

E.J. Calvo, E. Forzani, M. Otero. Analytical Chemistry, 74, 2002, 3281.



E.S. Forzani, M. Otero, M.A. Pérez, M. López Teijelo, E.J. Calvo, Langmuir, 18, 2002, 4020.

X-Ray Reflectivity

PAH – PSS on glass



FTIR-RAS wide spectra of $(PAH-Os)_{15}(PSS)_{14}$

Dry film in air



Observed frequencies / cm ⁻¹	Assignment		
1008	benzyl ring in PSS		
1035	-SO ₃ symmetric stretching		
1187	SO ₃ ° asymmetric stretching		
1216	SO ₃ ⁻ asymmetric stretching		
1420	pyridine in PAH-Os		
1460	-CH ₂ - deformation, aromatic and		
	pyridine stretchings		
1530	NH3 ⁺ symmetric deformation and		
	pyridine stretching		
1610	NH3 ⁺ asymmetric deformation and water		
	trapped deformation		
2929	Aliphatic – C-H stretchings		
3050	Aromatic -C-H stretching		
3430	NH3 ⁺ asymmetric and water		
	trapped stretching		

C. Bonazzola, E.J. Calvo, F.C. Nart, Langmuir, 19, 2003, 5279-5286.

Resonant Raman spectroscopy of PAH–Os self-assembled multilayers

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Dynamics on Redox Switching

CYCLIC VOLTAMMETRY











Electrodo Película Redox Electrolito





Electrodo Película Redox Electrolito















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E.S. Forzani, M.A. Perez, M. Lopez Teijelo, E.J. Calvo, Langmuir 2002

CHRONOAMPEROMETRY

Bound diffusion in the thin film







I / mA.cm⁻²

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)



0

2

log(f/Hz)

3

0

log(f/Hz)

Z'(ω) Z''(ω)

Z img / Ω

 \Box

M.E. Tagliazucchi, E.J. Calvo, J. Electroanalyt. Chem., (2006) in press.

Donnan Equilibrium



$$\Delta \phi_{\rm D} = \frac{\omega RT}{F} \ln \left[\frac{c_{\rm F} + (c_{\rm F}^2 + 4c_{\rm S}^2)^{1/2}}{2c_{\rm S}} \right]$$

 C_F : Fixed charges in the polymer C_s : Charges in solution

 $\Delta \phi_{\rm D}$: Donnan potential



Effect of specific ions exchanged



Fig. 1. Cyclic voltamperograms for (PAH-Os)₅(PVS)₄ electrode in NaCl 10mM (solid line) and NaClO₄ 10mM (dashed line). Scan rate: 25 mV.s⁻¹.

M. Tagliazucchi, E.J. Calvo, PCCP 2006, in press

ANIONS

CATIONS



M. Tagliazucchi, E.J. Calvo, PCCP 2006, in press





Table 3 End to end mass to charge relationships for data in Figures 3 and

NaCl

4.

Sodium salts	$\Delta m/\Delta q^{1}$ g.C ⁻¹ (x 10 ³)	∆m ¹ g.mol ⁻¹ (x 10 ³)	N _{H20}
NaC1	64±9	615±90	32
NaF	72 ± 9	692± 90	37
NaNO3	19±9	185± 90	7
NaBF4	20±9	195± 90	6
NaClO ₄	6 ± 9	58±90	-2.3
Chloride salts			
NaCl	62±9	598 ± 90	31
LiCl	62±9	596 ± 90	31
CsCl	58±9	564 ± 90	29
HCI	69±9	662 ± 90	35

¹Error was estimated from comparing measures in NaCl 10mM at different stages of the experiment.



M. Tagliazucchi, E.J. Calvo, PCCP 2006, in press



D.E. Grumelli, . Garay, C.A. Barbero, E.J. Calvo, J. Phys.Chem. B, 8 (2006) 1353-

"BREAK IN" EFFECTS



D. Grumelli, C. Barbero, E.J. Calvo, J. Phys. Chem. B, 8 (2006) 1353–1357

Solvent and ion dynamics







84

D. Grumelli, C. Bonazzola, E.J. Calvo, J. Phys. Chem. B, 8 (2006) 1353-1357

EQCM gravimentric response of (PAH-Os)₁₅(PSS)₁₄ film in 10 mM NaCl for repetitive potential steps from 0.1 to 0.6 V.



800

t/s

860

M.E. Tagliazucchi, E.J. Calvo, J. Electroanalyt. Chem., (2006) in press.

In situ SNIFTIR spectra in the H_2O absorption region for a sequence of oxidation-reduction steps of $(PAH-Os)_{15}(PSS)_{14}$ in 10 mM HCl from 0.1 to 0.6 V in the oxidized state Os(III)



$$\left[PAH - Os(II)^{+} PVS^{-}A^{-}C^{+} \right]_{poly} + xA_{aq}^{-} \rightarrow (1 - x) \left[PAH - Os(III)^{+2} PVS^{-}A^{-} \right]_{poly} + (1 - x)C_{aq}^{+} + x \left[PAH - Os(III)^{+2} PVS^{-}C^{+}2A^{-} \right]_{poly} + e(Au)$$

D. Grumelli, C. Bonazzola, E.J. Calvo, J. Phys. Chem. B, 8 (2006) 1353–1357

Evidence of Water accumulation in the LbL redox film by continuous oxidationreduction cycles







Fig. 4. Infrared absorbance at 1640 and 3400 cm⁻¹ as a function of the number of oxidation-reduction cycles of PAH-Os and PSS multilayer film. Inset: Variation of mass (EQCM) during repetitive oxidation-reduction cycles.

"Break in"

$$\left[PAH - Os(II)^{+}PVS^{-}\right]_{poly} + A_{aq}^{-} + nH_{2}O \rightarrow \left[PAH - Os(III)^{2+}PVS^{-}A^{-}nH_{2}O\right]_{poly} + e(Au)$$

Steady State

$$\left[PAH - Os(II)^{+} PVS^{-}A^{-}C^{+} \right]_{poly} + xA_{aq}^{-} \rightarrow (1-x) \left[PAH - Os(III)^{+2} PVS^{-}A^{-} \right]_{poly} + (1-x)C_{aq}^{+} + x \left[PAH - Os(III)^{+2} PVS^{-}C^{+}2A^{-} \right]_{poly} + e(Au)$$

D. Grumelli, C. Bonazzola, E.J. Calvo, Electrochem. Comm. 2006

Polymer charge controlled by acid-base equilibrium in weak polyelectrolytes

 $P-NH_2 + H^+ \leftrightarrow P-NH_3^+$



J. Choi, M.F. Rubner, macromolecules 2005.

We can regulate the thickness and structure of redox PEM multilayers by adjusting the charge density in the weak polyelectrolytes by controlling the pH of the PAH-Os solutions.



S.S. Shirartori, M.F. Rubner, Macromolecules, 2000, 33, 4213



(PAH-Os) (PVS) 450 800 8.3 • PAH-Os ∎pH = 8.75 400 700 GOx pH = 8.25 350 600 Thickness / nm 300 7.3 500 pH = 7.15 Thickness / nm 250 400 pH = 7.50 5.5 200 300 150 .5 200 100 pH = 5.50-100 50 · 0 0 -50 40 2 6 10 12 20 60 0 8 0 Δ layer number Layer number

M. Tagliazucchi, unpublished work

E. S.; Calvo, E. J.; Luduena, S. J.; Pietrasanta, L. I., Anal. Chem.; 2006; 78(2); 399-407.

Ellipsometry Thickness

Electrochemical Quartz Crystal Microbalance (EQCM)





Molecular Theory

bulk electrolyte solution



$$F = -TS_{pol} + F_{VdW} - TS_{s,mix} - TS_{A,mix} - TS_{C,mix} - TS_{H^+,mix} - TS_{OH^-,mix} + F_{NH_2/NH_3^+} + F_{OS(III)/OS(II)} + F_{Elec} + F_{OS(III)/OS(II)} + F_{OS(II)/OS(II)} + F_{OS(III)/OS(II)} + F_{OS(II)$$

$$\begin{split} &-\frac{S_{pol}}{Ak_{B}} = \frac{N_{P}}{A} \left[\sum_{\alpha} P_{P}(\alpha) \left[\ln P_{P}(\alpha) + \beta U_{PS}(\alpha) \right] \right] \\ &-\frac{\beta F_{VdW}}{A} = \frac{\chi}{2} \int \int \left[\langle n_{P}(z) \rangle v_{pol} + \langle n_{Os}(z) \rangle v_{Os} \left[\langle n_{P}(z') \rangle v_{pol} + \langle n_{Os}(z') \rangle v_{Os} \right] dz dz' \\ &-\frac{S_{i,mix}}{Ak_{B}} = \int \rho_{i}(z) \left[\ln(\rho_{i}(z)v_{i}) - 1 \right] dz \\ &\frac{\beta F_{NH_{2}/NH_{3}^{+}}}{A} = \int \langle n_{P}(z) \rangle \left(f(z) \left[\ln(f(z)) + \beta \mu_{BH_{+}}^{0} \right] + (1 - f(z)) \left[\ln(1 - f(z)) + \beta \mu_{B}^{0} \right] dz \\ &\frac{\beta F_{Os(III)/Os(II)}}{A} = \int \langle n_{Os}(z) \rangle \left(f_{Os}(z) \left[\ln(f_{Os}(z)) + \beta \mu_{Os(III)}^{0} \right] + (1 - f_{Os}(z)) \left[\ln(1 - f_{Os}(z)) + \beta \mu_{Os(II)}^{0} \right] dz \\ &\beta \left[e | \psi_{M} - \mu_{e(M)} \rangle \right] \left\langle n_{Os}(z) \rangle f_{Os}(z) dz \\ &\frac{\beta F_{Elec}}{A} = \beta \int \left[\rho_{Q}(z) \psi(z) + \frac{1}{2} \varepsilon \left(\frac{\partial \psi(z)}{\partial z} \right)^{2} \right] dz \end{split}$$

$$\langle n_P(z) \rangle = \frac{N_P}{A} \sum_{\alpha'} P_P(\alpha) n_P(z,\alpha)$$

$$\langle n_{Os}(z)\rangle = \frac{N_P}{A} \sum_{\alpha} P_P(\alpha) n_{Os}(z,\alpha)$$

$$\sum v_i \rho_i(z) + \langle n_P(z) \rangle v_{pol} + \langle n_{Os}(z) \rangle v_{Os} = 1$$











Ion Fluxes



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In Conclusion,

- LbL self-assembled redox polyelectrolyte multilayers allow:
- a) Control of film thickness in the nanoscale on flat surfaces and nanoparticles
- b) Control of surface charge
- c) Control of film structure and organization
 - Dynamics of Redox Switching dependent on the structure, thickness and charge in the topmost layer