

**LATTICE-GAS MODELS OF
ELECTROCHEMICAL ADSORPTION:
STATIC AND DYNAMIC ASPECTS**

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OBJECTIVES

- Study phase transitions in submonolayer electrosorption by computational lattice-gas modeling and experiments.
- Develop lattice-gas models from thermodynamic and structural data.
- Near-equilibrium studies:
 - Ground-state and phase diagrams.
 - CV for slow scan rates.
 - Estimate effective model parameters.
- Far-from equilibrium studies:
 - Current transients in potential-step experiments.
 - CV for fast scan rates.

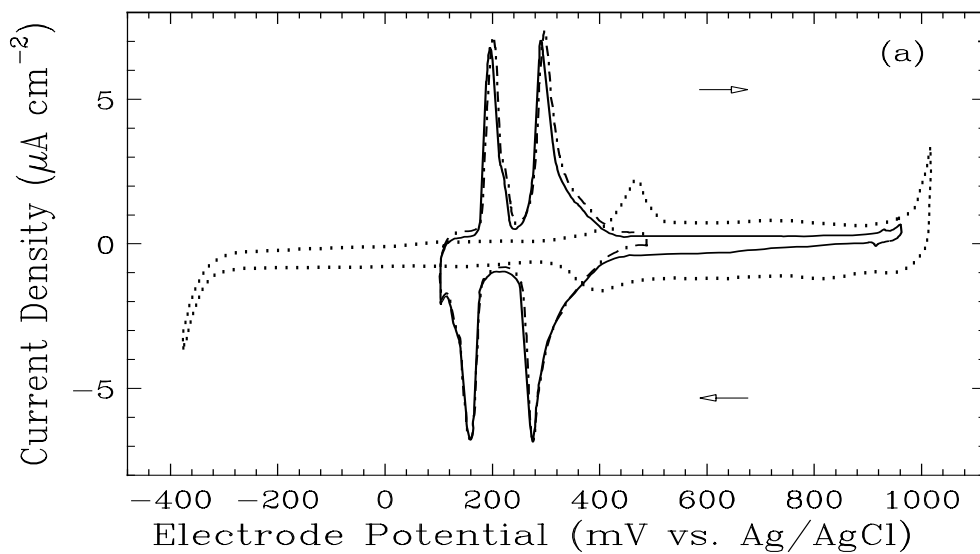
SPECIFIC SYSTEMS STUDIED

- Near equilibrium:
 - Urea on Pt(100) in perchloric acid.
 - UPD of Cu on Au(111) with sulfate.
- Far from equilibrium:
 - Simulated current transients in UPD potential-step experiments.

UREA ON Pt(100) AND Cu UPD NEAR EQUILIBRIUM

COMMON EXPERIMENTAL FEATURES

- Dramatic reduction of CV peak width(s) as adsorbate is added to the electrolyte.



- Ordered submonolayer adsorbate phases in limited potential range.
- Both narrowing and ordering strongly dependent on crystal plane and electrolyte.

COMMON THEORETICAL INTERPRETATION

1. Phase transition between cation covered surface for negative potentials and ordered submonolayer on positive side.
2. Geometric fit between adsorbate and adsorption sites important.

COMMON THEORETICAL MODEL

Two-component lattice-gas Hamiltonian:

$$\begin{aligned} \mathcal{H} = & - \sum_n \sum_{\langle ij \rangle}^{(n)} [\Phi_{AA}^{(n)} c_i^A c_j^A + \Phi_{AB}^{(n)} (c_i^A c_j^B + c_i^B c_j^A) \\ & + \Phi_{BB}^{(n)} c_i^B c_j^B] + \mathcal{H}_3 - \sum_i [\bar{\mu}_A c_i^A + \bar{\mu}_B c_i^B] \end{aligned}$$

$c_i^X \in \{0,1\}$: Local occupation variable for species X

$\Phi_{XY}^{(n)}$: n th-neighbor effective XY pair interaction

\mathcal{H}_3 : Multi-particle interactions

Electrochemical potentials:

$$\bar{\mu}_X = \mu_X^0 + RT \ln ([X]/[X]^0) - z_X F E$$

R : gas constant

T : temperature

F : Faraday's constant

z_X : effective electrovalences

μ_X^0 and $[X]^0$: reference values

E : Electrode potential

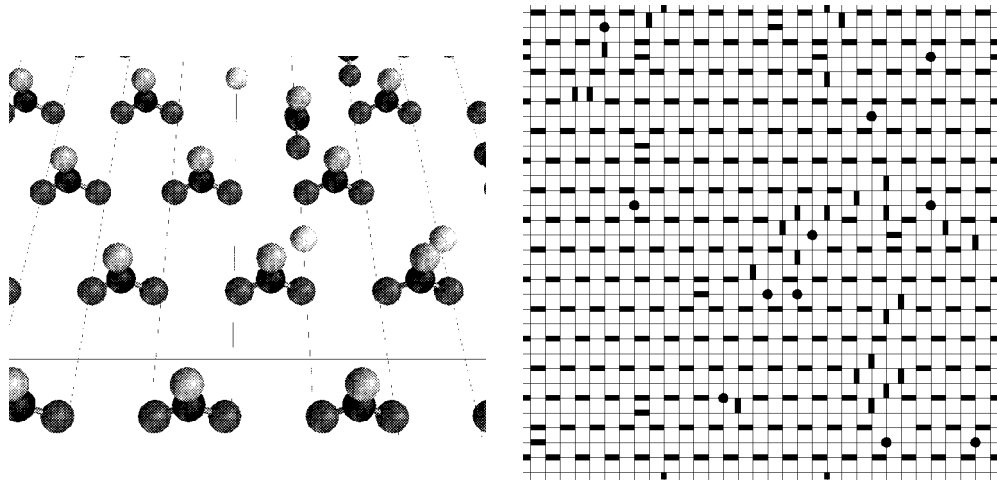
VOLTAMMETRIC CURRENT NEAR EQUILIBRIUM

Under quasi-equilibrium conditions and neglecting diffusion and double-layer capacity, the CV currents are proportional to the potential scan rate and can be obtained in terms of the lattice-gas response functions:

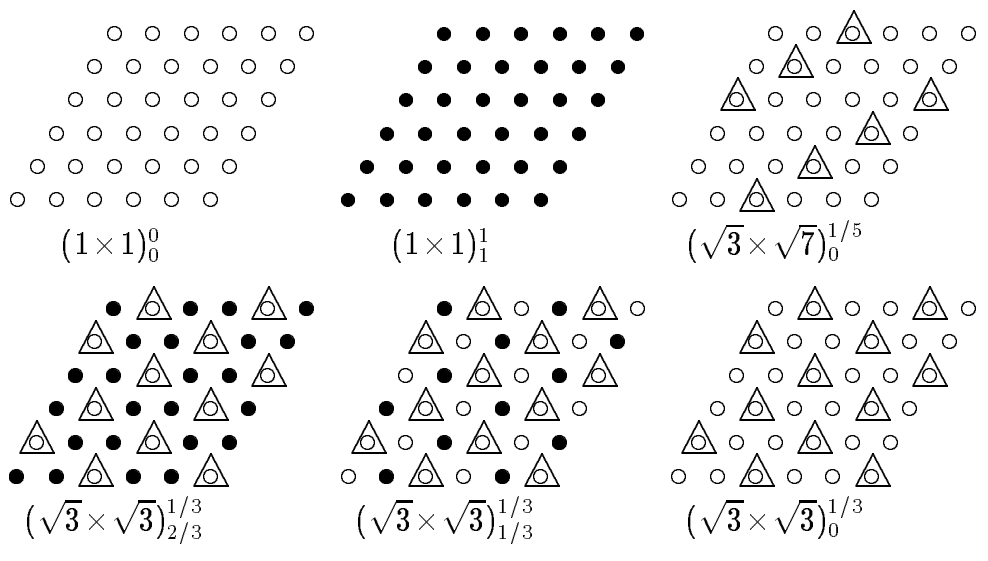
$$i = eF \left\{ z_A^2 \frac{\partial \Theta_A}{\partial \bar{\mu}_A} + 2z_A z_B \frac{\partial \Theta_B}{\partial \bar{\mu}_A} + z_B^2 \frac{\partial \Theta_B}{\partial \bar{\mu}_B} \right\} \frac{dE}{dt}$$

e : Elementary charge unit.

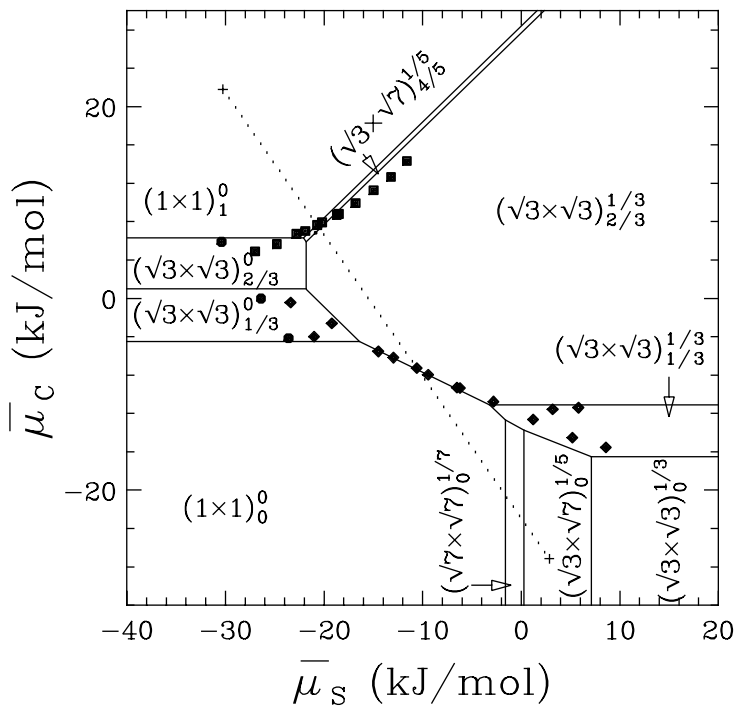
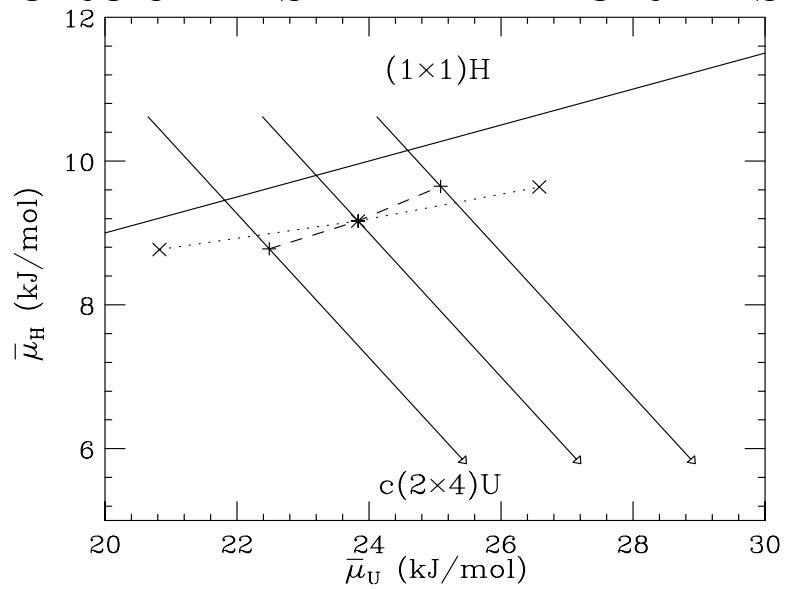
Θ_X : Surface coverage of X in ML.



SPECIFIC MODELS

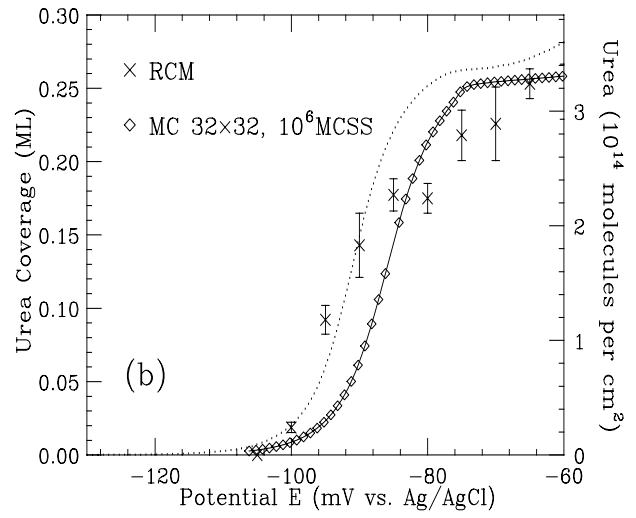
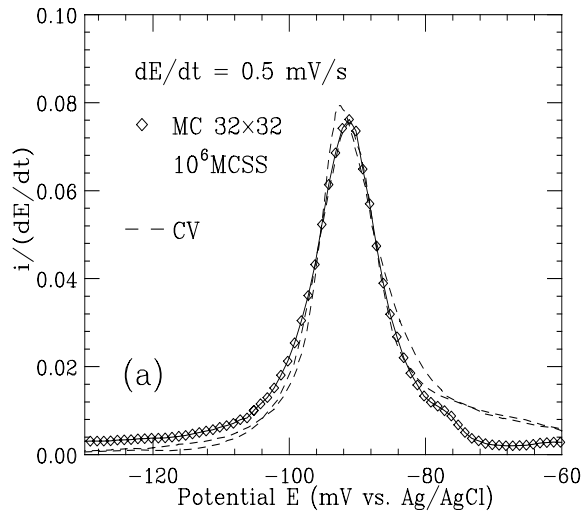


GROUND-STATE DIAGRAMS

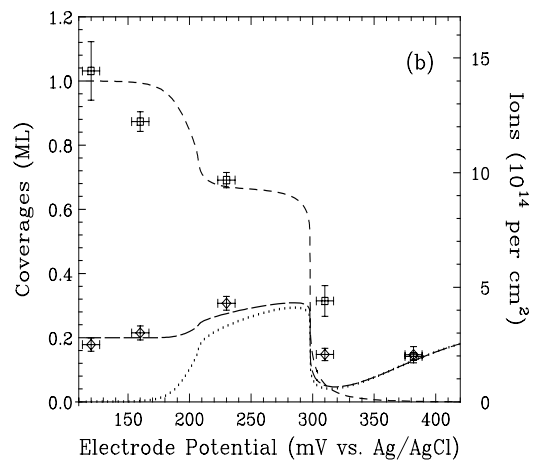
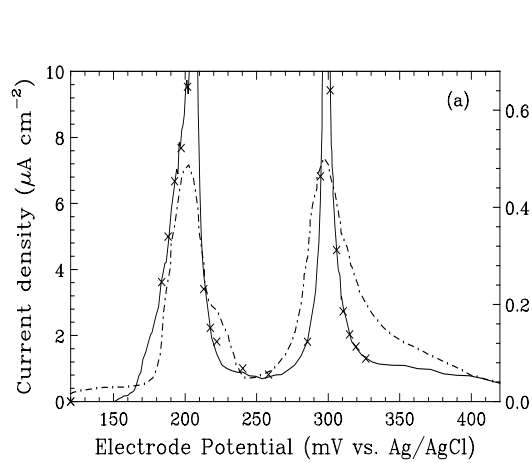


CV AND COVERAGES

Urea:



UPD of Cu on Au(111) with sulfate:



**RELAXATION FAR FROM
EQUILIBRIUM**
A SIMPLE MODEL FOR CURRENT
TRANSIENTS IN UPD

Typical potential-step experiments.

Cu UPD from Hölzle, Retter, and Kolb,
J. Electroanal. Chem. **371**, 101 (1994).

Lattice-gas model equivalent to kinetic Ising
ferromagnet with heat-bath dynamics

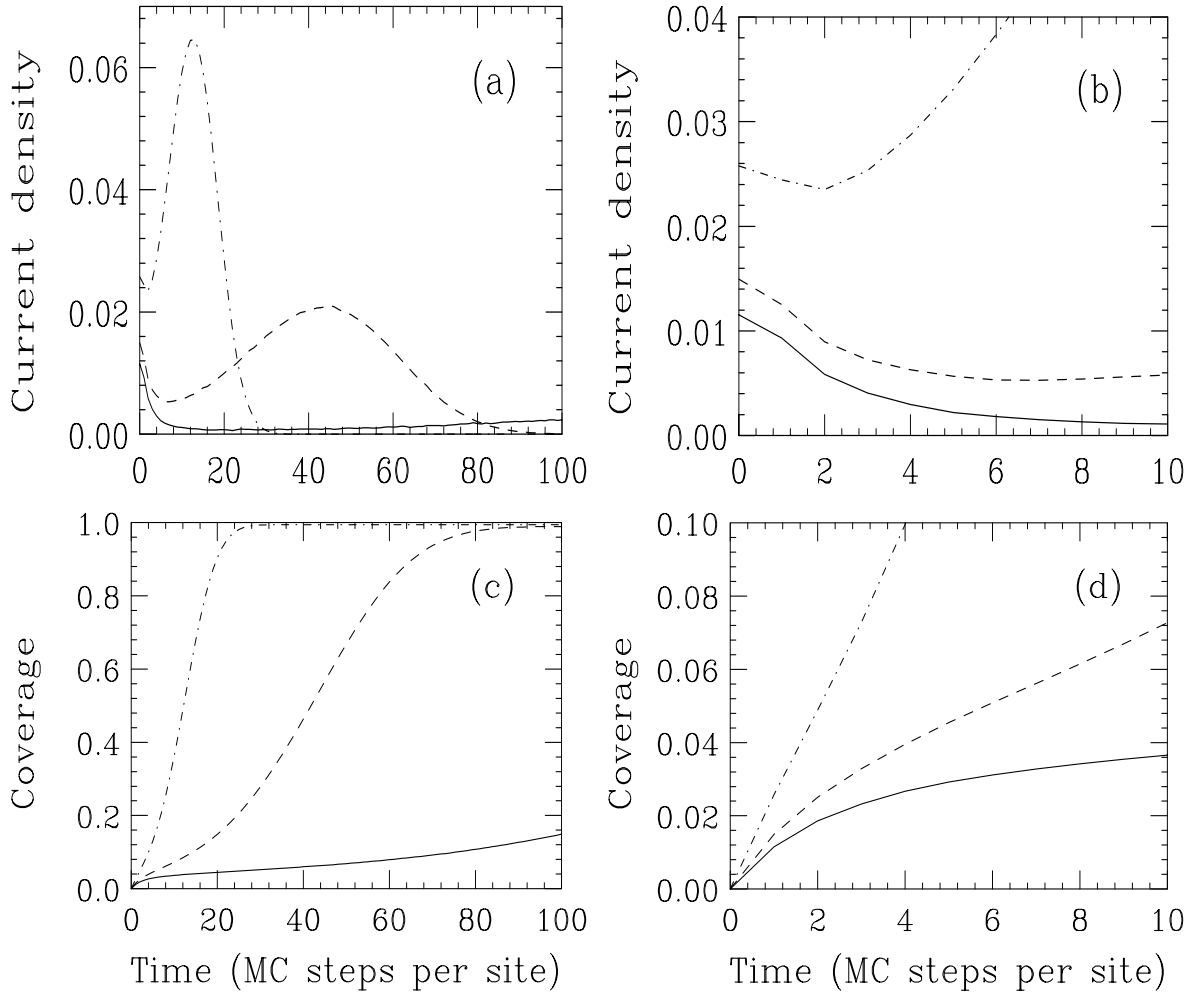
Hamiltonian:

$$\mathcal{H} = - \sum_{\langle ij \rangle} \Phi_{AA}^{(1)} c_i^A c_j^A - \sum_i \bar{\mu}_A c_i^A$$

Transition probabilities:

$$W(c_i^A \rightarrow c_i^A \prime) = \frac{\exp[-\Delta\mathcal{H}/k_B T]}{1 + \exp[-\Delta\mathcal{H}/k_B T]}$$

Numerical results



$T = 0.8T_c = 300\text{K}$ gives $\Phi_{AA}^{(1)} \approx 57\text{meV}$.

ΔE approximately $5.7\text{mV}/z_A$ (solid), $11.4\text{mV}/z_A$ (dashed), $22.8\text{mV}/z_A$ (dot-dash).

SUMMARY

- Developed microscopic models for urea adsorption on Pt(100) and UPD of Cu on Au(111) with sulfate, using thermodynamic and structural data.
- Near-equilibrium studies:
 - Obtained ground-state and phase diagrams.
 - Simulated CV profiles for slow scan rates.
 - Estimated effective model parameters.
- Far-from equilibrium studies:
 - Modeled current transients in potential-step experiments with simple kinetic model.
- Future plans:
Kinetic studies of models for specific systems, such as urea on Pt(100) and UPD of Cu with sulfate on Au(111).