

# **Phase Transitions in Electrochemical Adsorption**

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## OBJECTIVES

Coordinated studies of electrosorbed monolayers of small organics and ions on single-crystal surfaces of catalytically active metals by computational lattice-gas modeling and experiments.

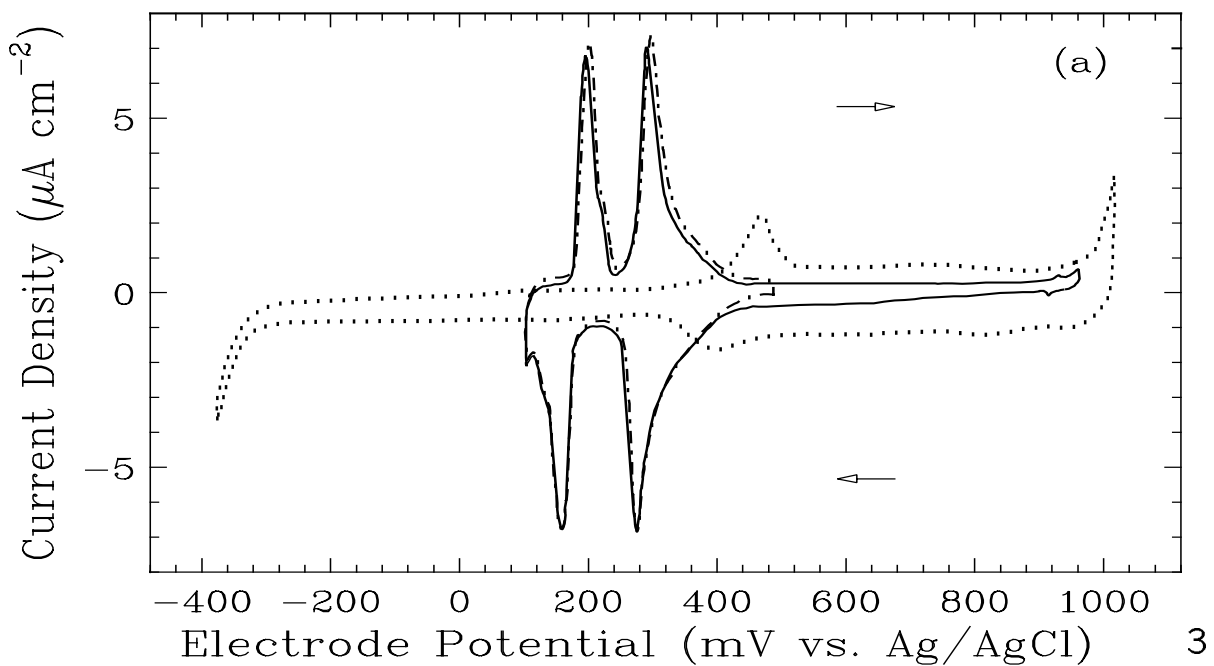
Develop lattice-gas models and estimate effective interaction energies from experimental thermodynamic and structural data.

### SPECIFIC EXAMPLES DISCUSSED:

- Urea on Pt(100) in perchloric acid.
- Underpotential Deposition (UPD) of Cu on Au(111) in sulfuric acid.

## COMMON EXPERIMENTAL FEATURES

- Dramatic reduction of CV peak width(s) as adsorbate (urea or  $\text{Cu}^{2+}$ ) is added to the electrolyte.



- Ordered, submonolayer adsorbate phases in limited potential range observed by *ex situ* and *in situ* methods.
- Both CV peak narrowing and ordering less pronounced on other crystallographic planes of the same metals, or with different electrolytes.

## COMMON THEORETICAL INTERPRETATION

1. Phase transition between cation covered surface on negative side of CV peak(s) and ordered submonolayer on positive side.
2. Geometric fit between adsorbate and adsorption sites important.

## COMMON THEORETICAL MODEL

Three-state lattice-gas Hamiltonian with intermediate-range and multi-particle interactions:

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

$c_i^{\text{X}} \in \{0,1\}$ : Local occupation variable for  
X=A or B.

$\Phi_{\text{XY}}^{(n)}$ : Effective XY pair interaction through  
 $n$ th-neighbor bond.

$\mathcal{H}_3$ : Multiparticle interactions.

$\bar{\mu}_{\text{X}}$ : Electrochemical potentials.

Relation of electrochemical potentials to experimental variables (weak-solution approximation):

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

$R$ : Molar gas constant.

$T$ : Absolute temperature.

$[X]$ : Bulk concentration of X.

$z_X$ : Effective electrovalence of X.

$F$ : Faraday's constant.

$E$ : Electrode potential.

$\bar{\mu}_X^0$  and  $[X]^0$ : Reference values containing binding energies.

CV current in limit of small  $dE/dt$ , neglecting diffusion and double-layer capacity:

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

$e$ : Elementary charge unit.

$\Theta_X$ : Surface coverage of X in ML.

## COMMON THEORETICAL PROCEDURE

1. Formulate specific lattice-gas model, considering local adsorption geometry.
2. Use experimental information to determine the adsorbate phases.
3. Perform group-theoretical ground-state calculation ( $T=0$  phase diagram) to find lattice-gas interaction ranges consistent with experiments.
4. Calculate coverages, order parameters, and CV currents by Monte Carlo simulation.
5. Vary the lattice-gas parameters to obtain optimal agreement with experiments.
6. Suggest further experiments, based on model predictions.
7. Return to 1, ..., 5 to accommodate new experiments.
8. Iterate until publishable.

UREA ELECTROSORPTION ON Pt(100)  
Experimental reminder

## Specific experimental results:

1. Urea coverage  $\Theta_U$  measured by *in situ* radiochemical method (RCM).  
Change: 0 to  $\approx 1/4$ ML over  $\approx 20$ mV.
2. *Ex situ* AES consistent with RCM.
3. *Ex situ* LEED shows unreconstructed ( $1 \times 1$ ) Pt(100) structure on negative side and  $c(2 \times 4)$  adsorbate structure on positive side of CV peak.
4. CV peak potentials measured vs [U] between 0.3 and 3.0mM.
5. CV performed between 0°C and 40°C.

## Observations:

- Assume Urea [ $\text{CO}(\text{NH}_2)_2$ ] coordinates Pt through Nitrogen (or  $\text{NH}_2$ ), with  $\text{C}=\text{O}$  group vertical.
- Urea N-N distance matches Pt(100) lattice constant ( $2.33\text{\AA}$  vs  $2.77\text{\AA}$ ).
- Coulometry: Most of the H desorbs as Urea adsorbs.

## Resulting model:

Urea (A) on bonds and H (B) on nodes of square lattice.

Effective interactions out to 8-th nearest neighbors stabilize  $c(2\times 4)$  phase.

# Model and configurations

# Phase diagrams

## CV and RCM

## Effective interactions (in kJ/mol)

$$\Phi_{HH}^{(1)} = -2.0$$

$$\Phi_{HU}^{(1)} = -8.0, \quad \Phi_{HU}^{(2)} = -4.0$$

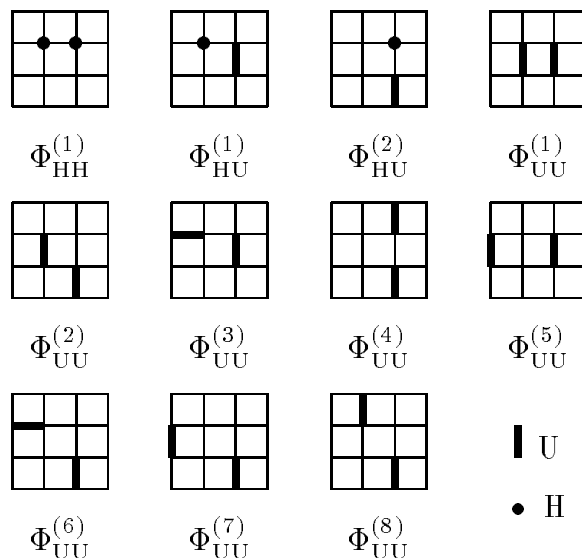
$$\Phi_{UU}^{(1)} = -13.0, \quad \Phi_{UU}^{(2)} = -10.0$$

$$\Phi_{UU}^{(3)} = -5.9, \quad \Phi_{UU}^{(4)} = -0.5$$

$$\Phi_{UU}^{(5)} = -2.5, \quad \Phi_{UU}^{(6)} = -3.0$$

$$\Phi_{UU}^{(7)} = +0.25, \quad \Phi_{UU}^{(8)} = -2.0$$

$$z_H = +1, \quad z_U = -1$$



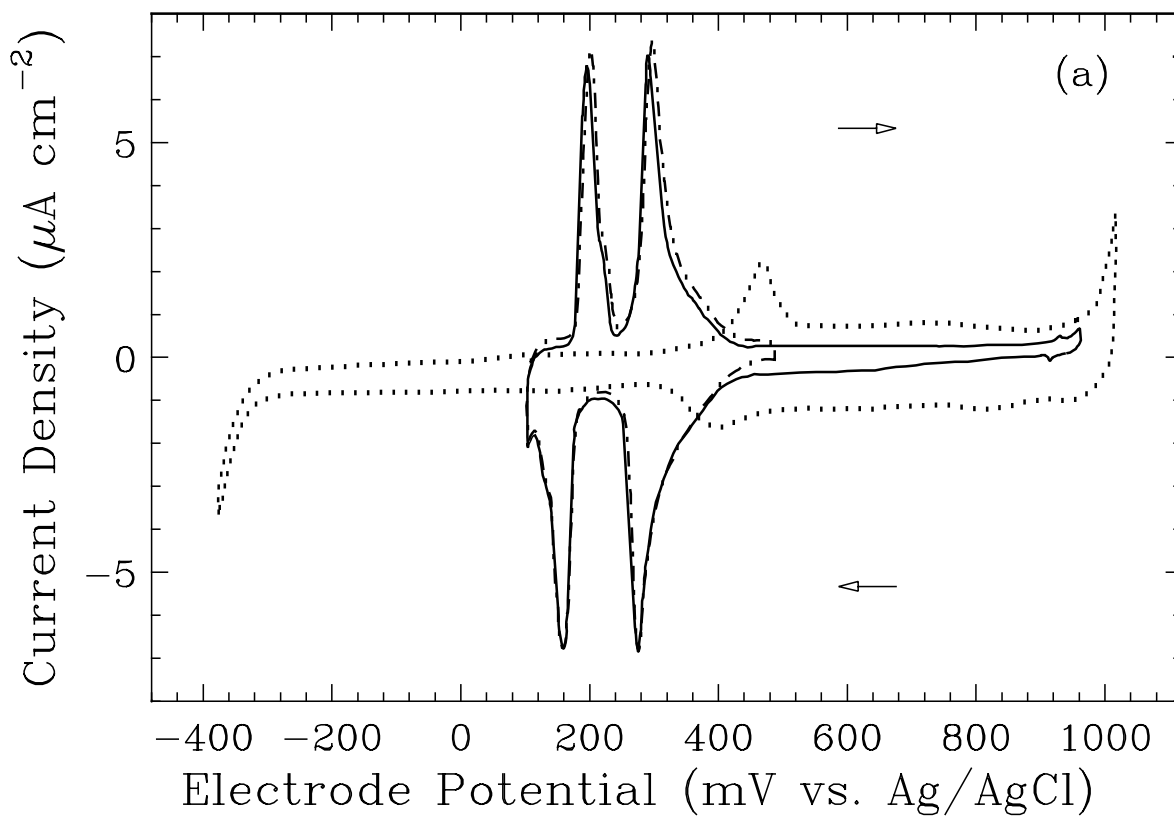
## Temperature effects

## Temperature effects. Interpretation.

- No statistically significant  $T$ -dependence in peak width, height, or position.
- Highly statistically significant, six-fold decrease in peak separation by increasing  $T$  from  $0^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ .
- The temperature effects likely kinetic.
- What about the sharp order-disorder peak in MC at  $10^{\circ}\text{C}$ ?
- Suggested answer: Not observed experimentally because of critical slowing down.

# UPD OF Cu WITH SULFATE ON Au(111)

## Experimental reminder



## Specific experimental results:

1. Two sharp CV peaks, *ca.* 100 mV apart, emerge when  $> 0.1$  mM Cu added to 0.1 mM sulfate electrolyte.
2. Cu and sulfate coverages measured by *ex situ* AES: Mixed  $2/3$  Cu +  $1/3$  sulfate between the peaks.
3. *Ex situ* LEED (by us) and *in situ* X-ray diffraction (by others) indicate  $(\sqrt{3} \times \sqrt{3})$  structure between the peaks.
4. Cu monolayer left of left peak. No Cu right of right peak;  $(\sqrt{3} \times \sqrt{7})$  sulfate layer?
5. CV peak potentials measured by others vs  $\text{Cu}^{2+}$  concentration between 0.5 and 50 mM. Allows calculation of effective electrovalences,  $z_C$  and  $z_S$ .

## Observations:

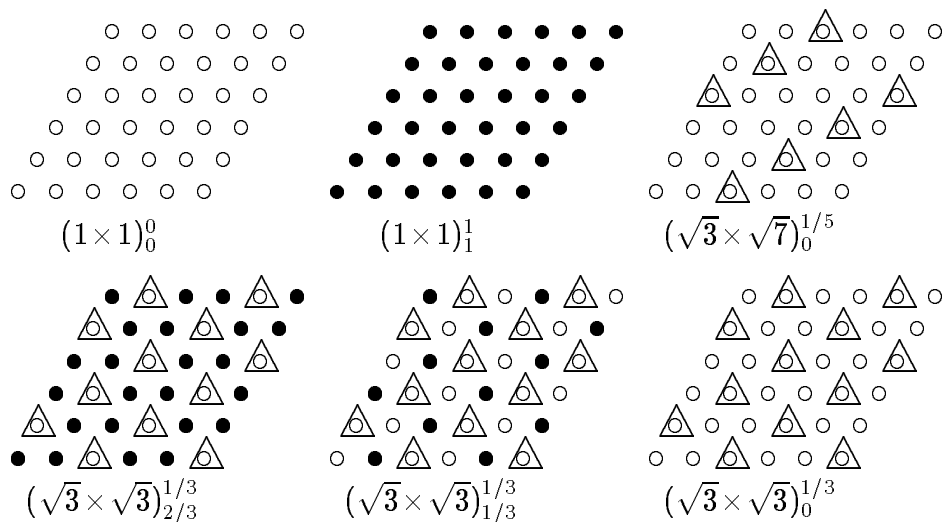
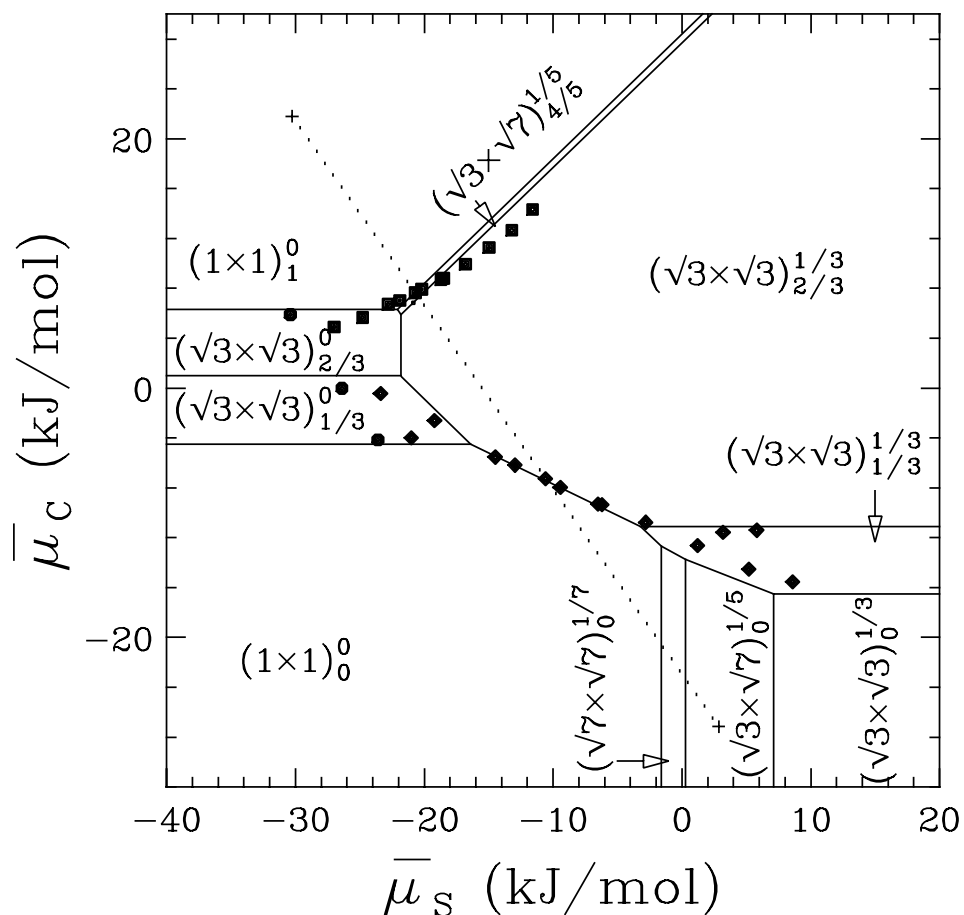
- Assume Sulfate ( $\text{SO}_4^{2-}$ ) coordinates Au(111) through three Oxygen atoms, with fourth S-O bond vertical.
- Sulfate O-O distance matches Au(111) lattice constant ( $2.4\text{\AA}$  vs  $2.88\text{\AA}$ ). Both adsorbate and substrate have triangular symmetry.
- Coulometry: Cu desorbs in two steps at CV peaks as sulfate adsorbs.

## Resulting model:

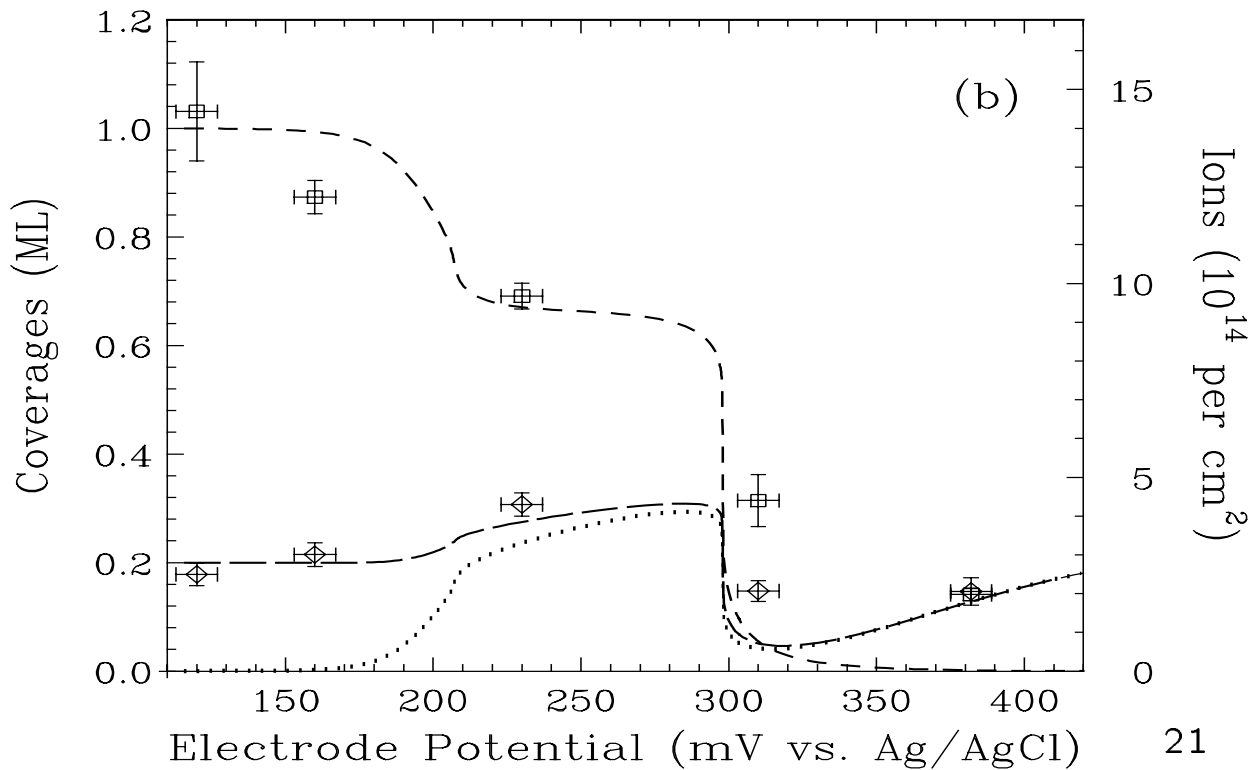
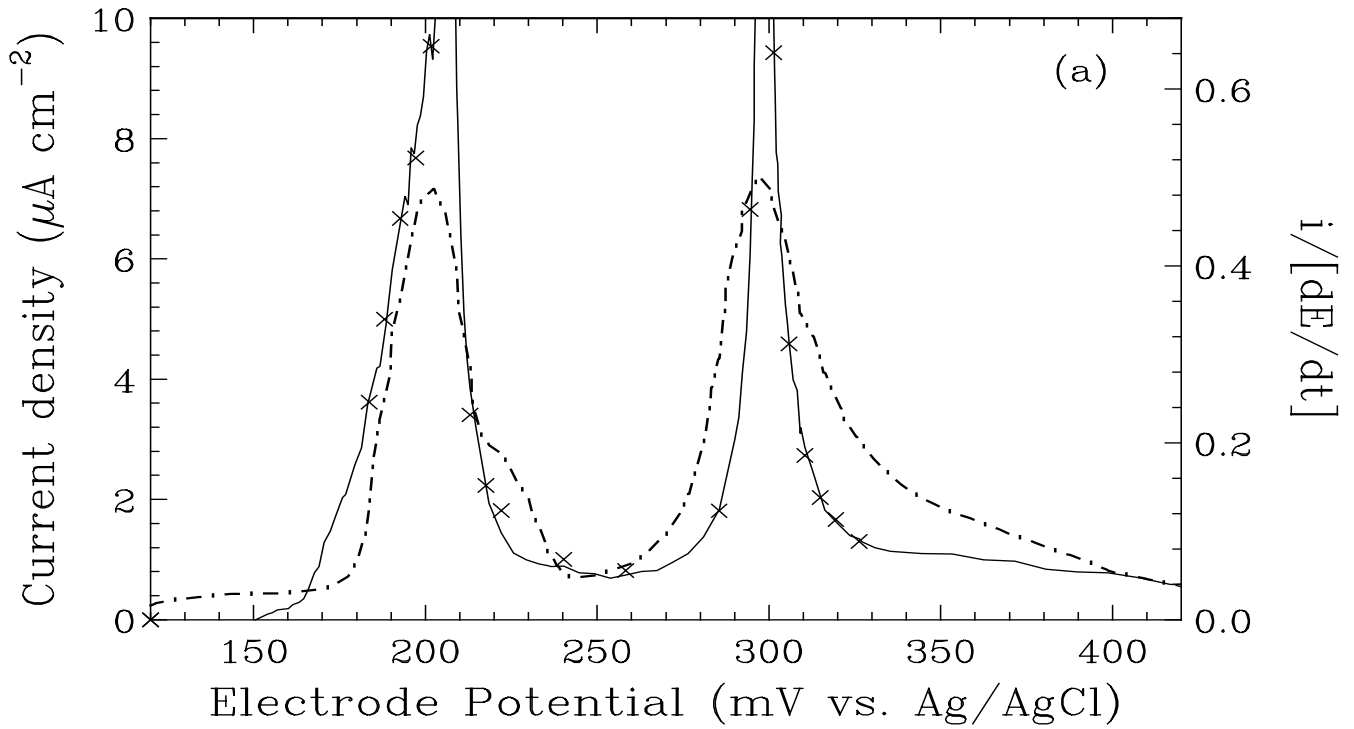
Sulfate (A) as hard hexagons and Cu (B) as point particles on triangular lattice.

Effective interactions out to 4-th nearest neighbors stabilize  $(\sqrt{3} \times \sqrt{7})$  sulfate phase.

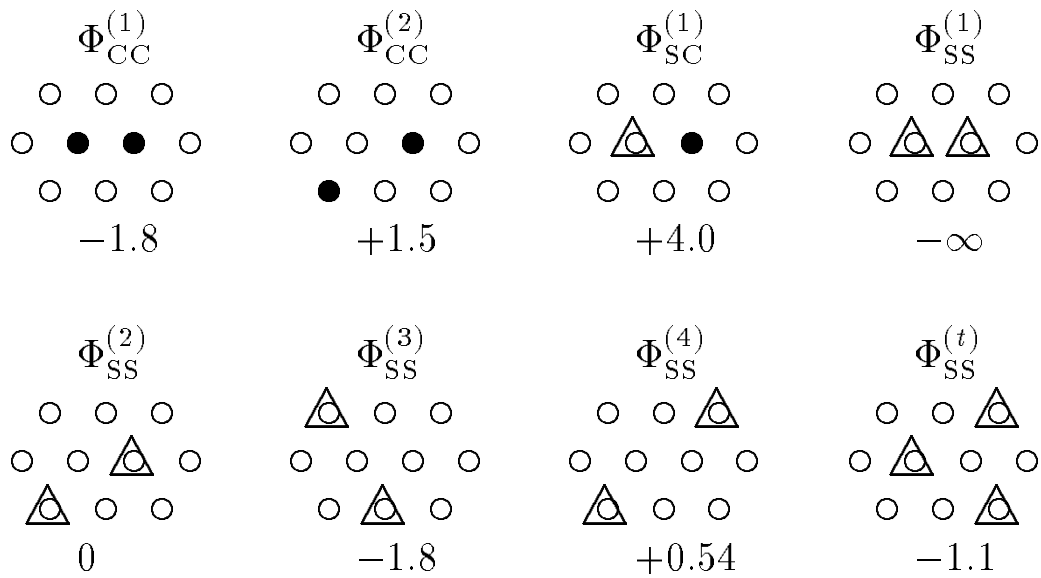
# Phase diagram and configurations



# CV current and Coverages



## Effective interactions (In kJ/mol)



## CONCLUSIONS:

- Relatively simple lattice-gas models can describe ordering and fluctuations in electrochemical adsorbate systems.
- Approximate, effective interactions that cannot yet be calculated from first principles can be obtained by adjusting numerically obtained lattice-gas predictions to a variety of experimental results.
- Demonstrated the importance of local bonding geometry. Can help predict which systems will have commensurate, ordered adsorbate phases.
- Interesting, temperature-dependent kinetic effects are awaiting further study.