Charge-Enhanced Dry Impregnation: A Simple Way to Improve the Preparation of Supported Metal Catalysts

Xiaoru Zhu, Hye-ran Cho[1], Malini Pasupong, and John R. Regalbuto[1]

Department of Chemical Engineering (m/c 110), University of Illinois at Chicago, 810 S Clinton Street, Chicago, Illinois, 60607
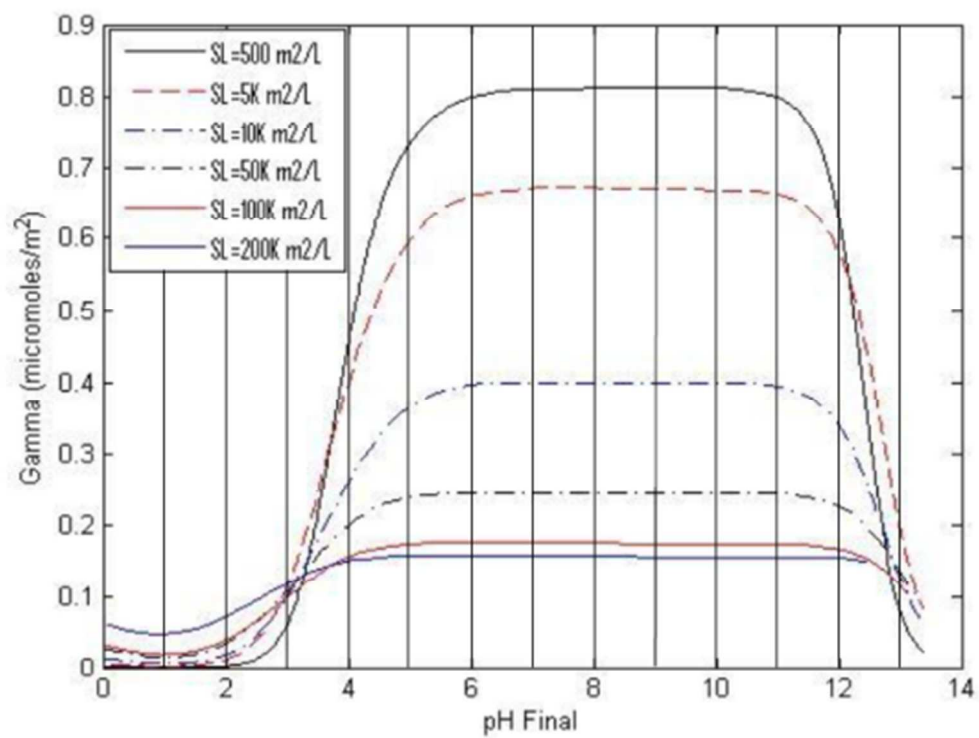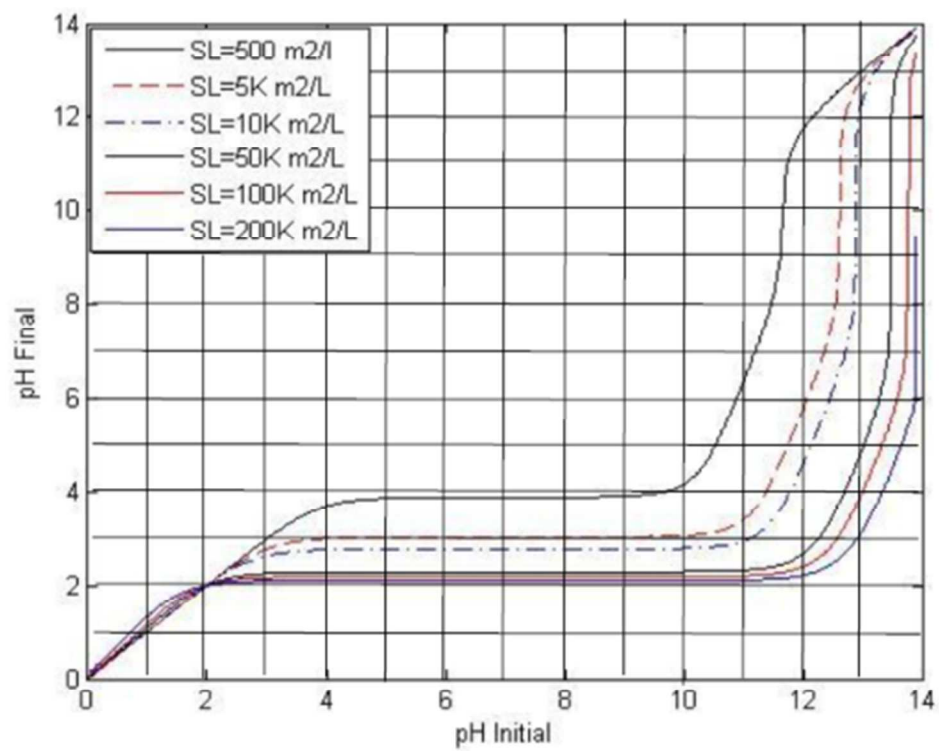
[1] Department of Chemical Engineering , University of South Carolina, 301 Main Street, Columbia, South Carolina, 29208
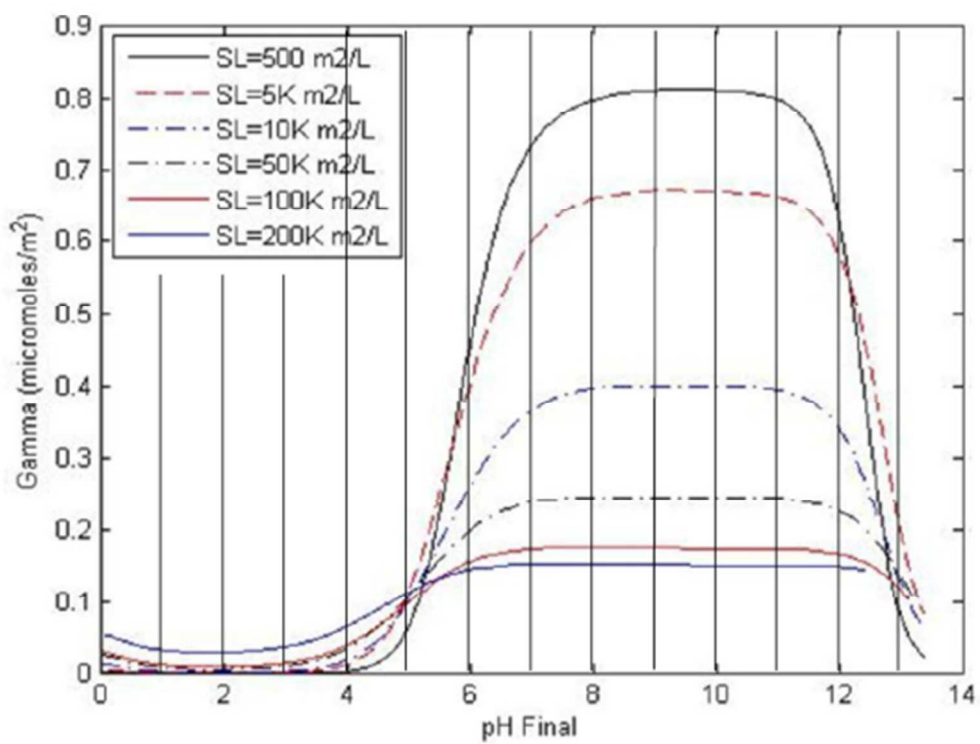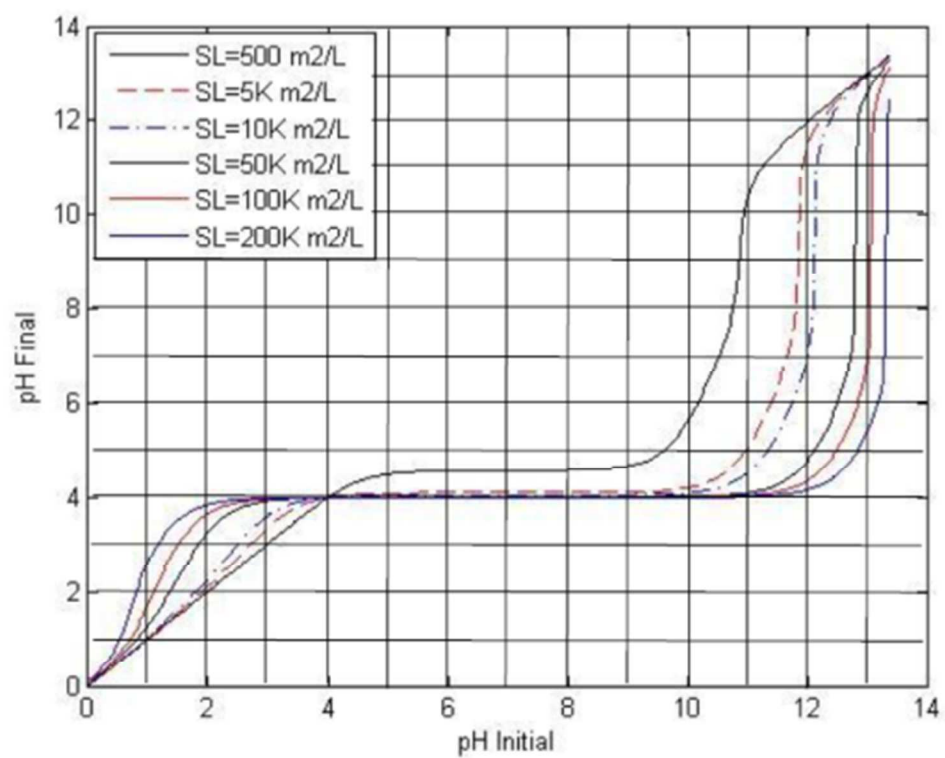
Email : regalbuj@cec.sc.edu

SUPPORTING INFORMATION 1.

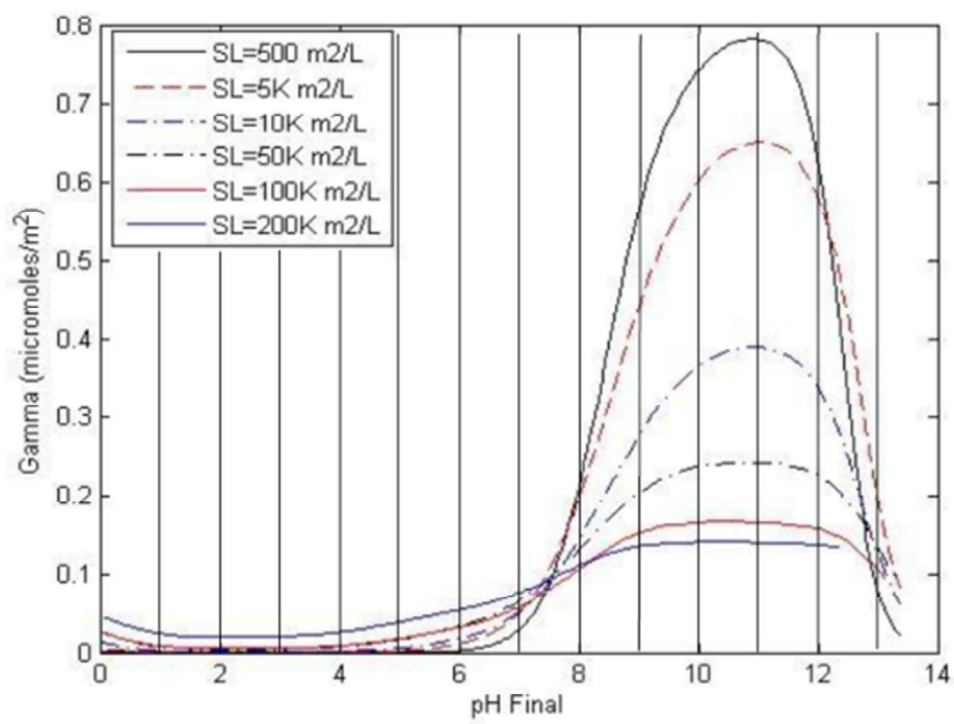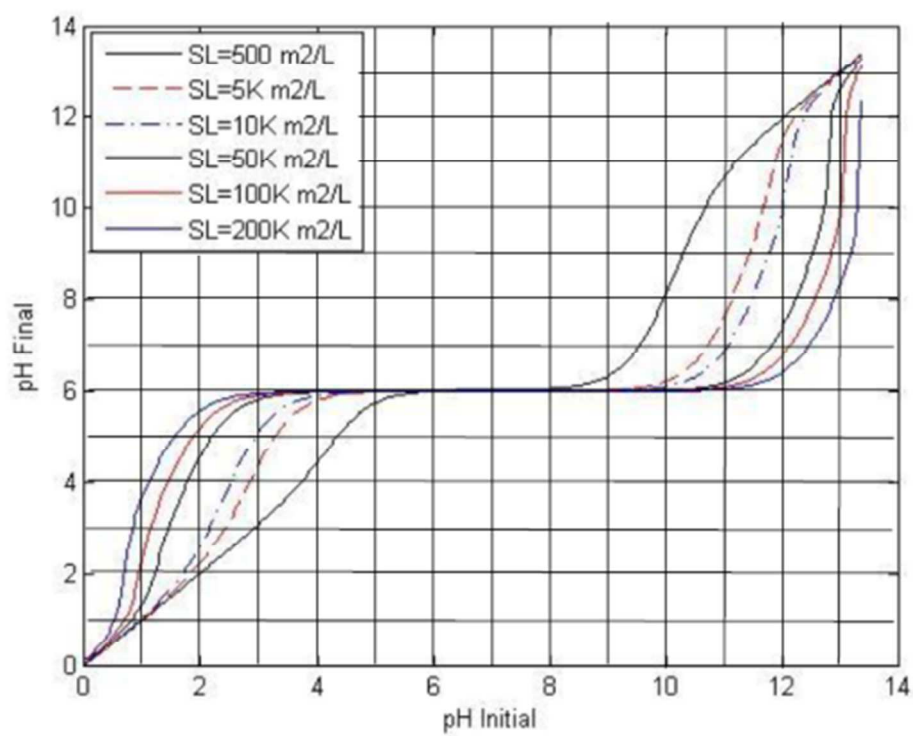Figure S1 a-f.Graphs for selection of initial pH based on support PZC and surface loading.
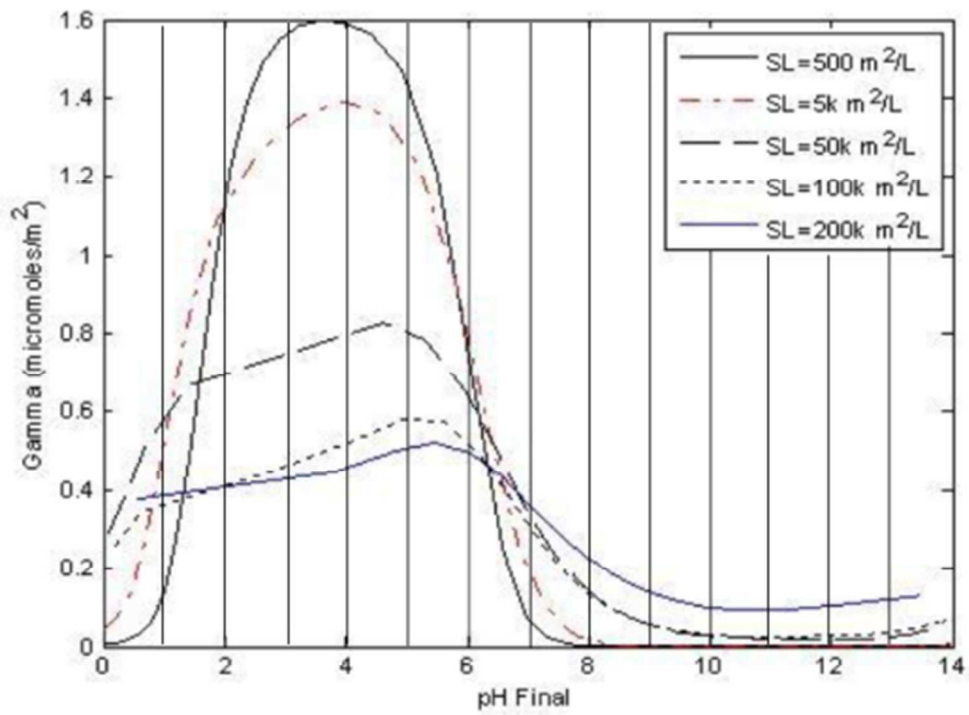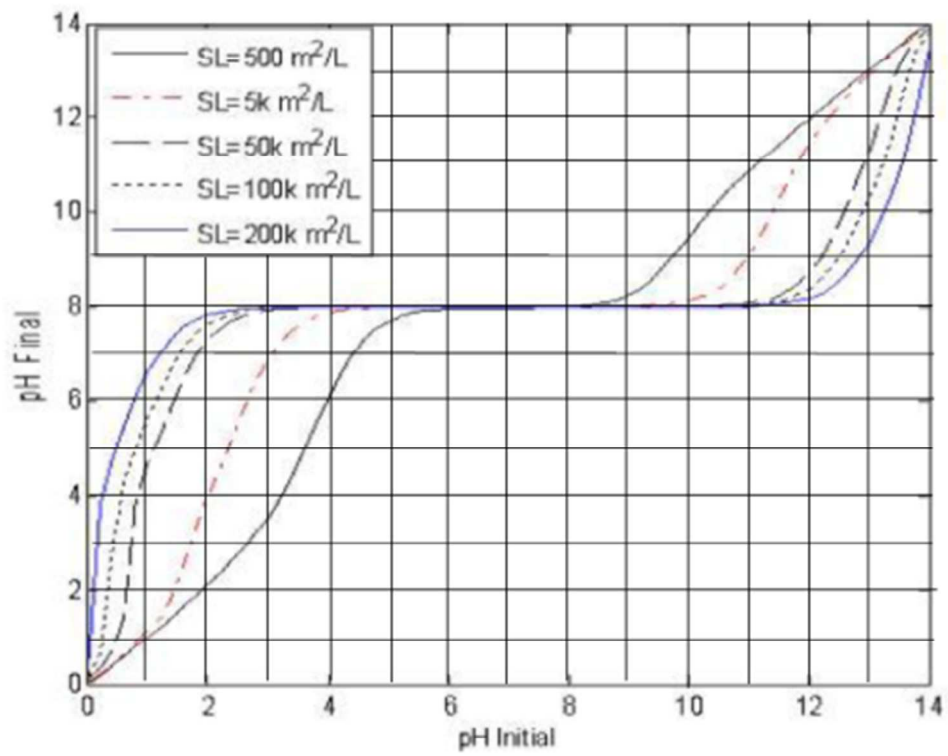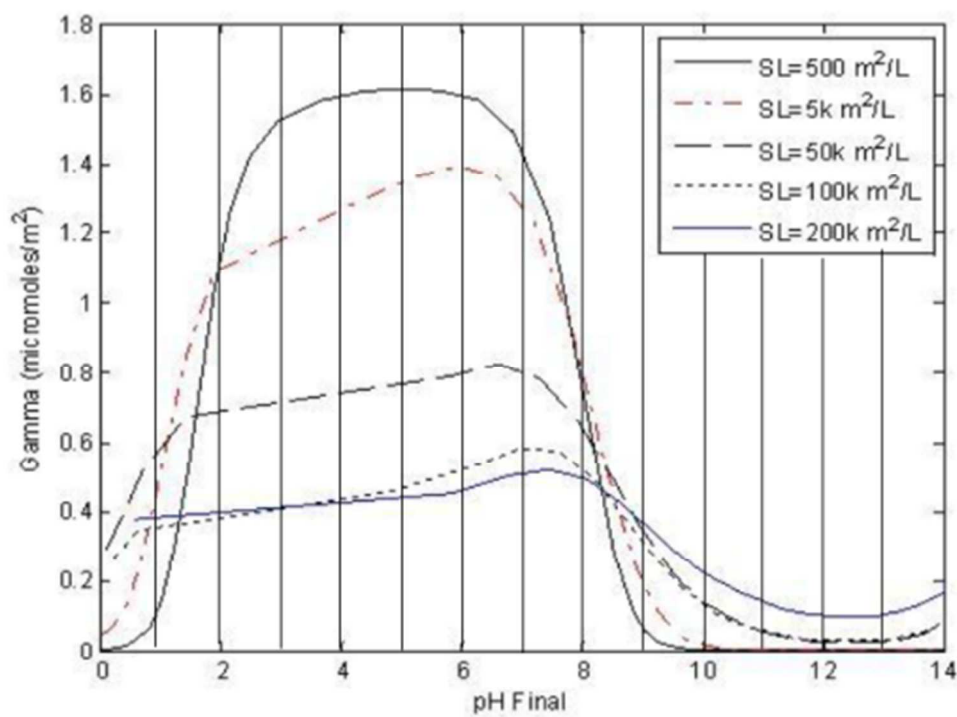
a. Model one site, two dpk PZC 2
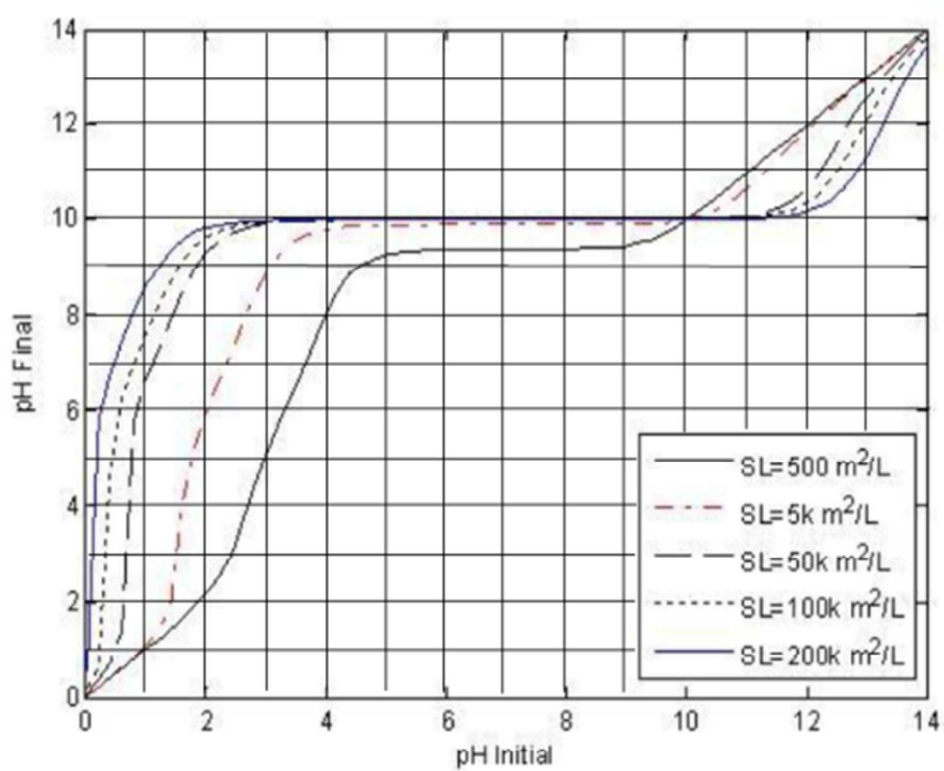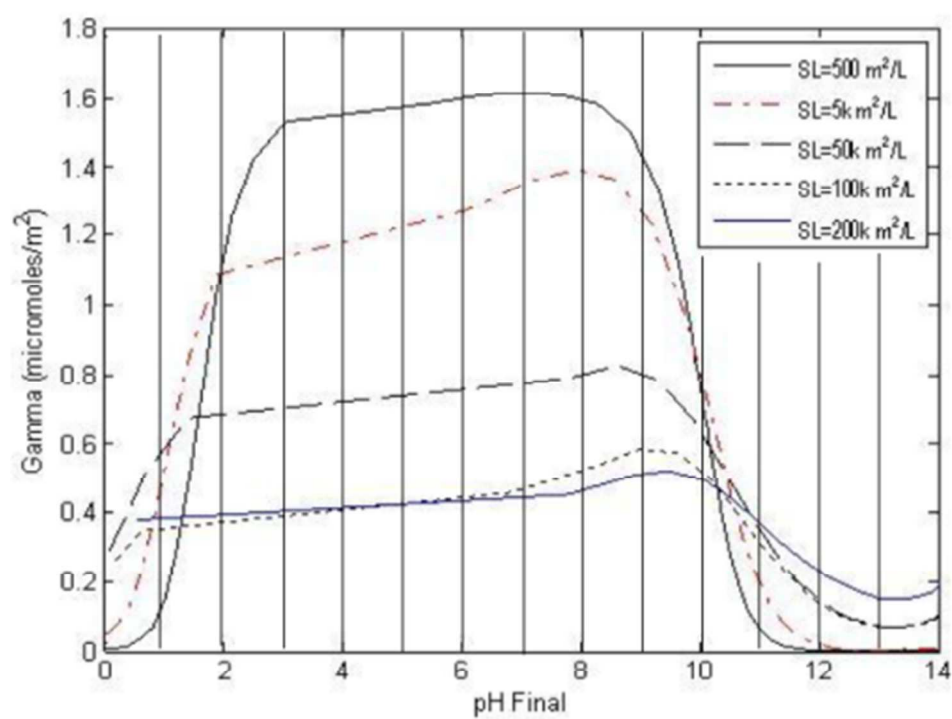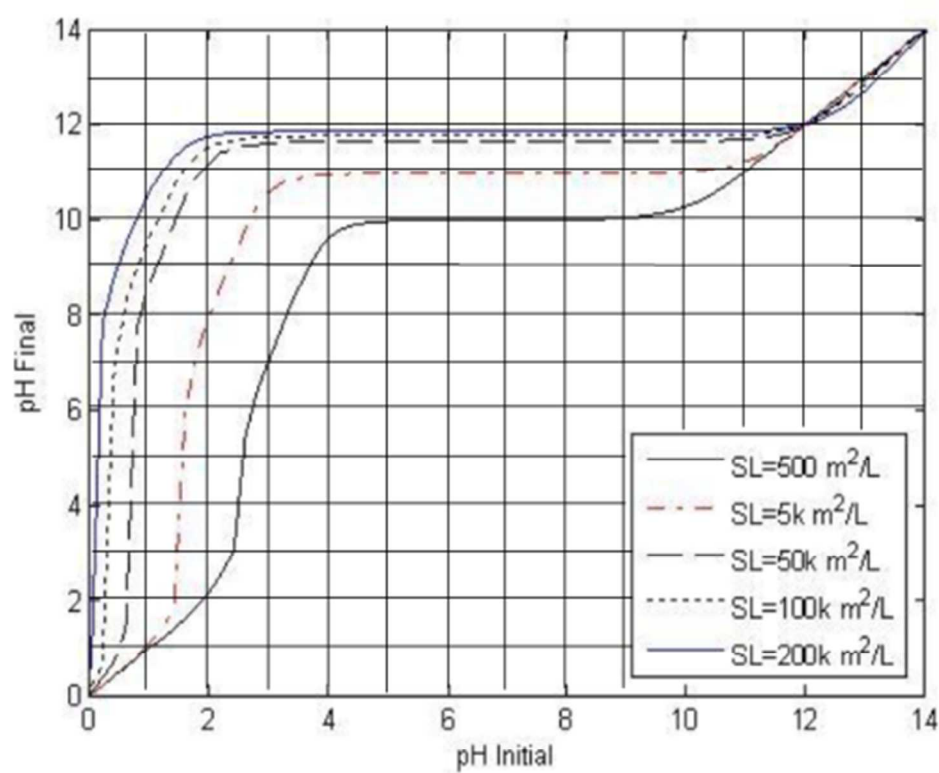
b. PZC 4

c. PZC 6

d. PZC 8

e. PZC 10

f. PZC 12

SUPPORTING INFORMATION 2: Revised Physical Adsorption (RPA) Model

- pH shift model

On the oxide surface (as shown in figure 1), the surface hydroxyl groups protonate or deprotonate as a function of the solution pH. At low pH, the surface is positively charged; on the other hand, at high pH, the surface is negatively charged. Assuming the single site, two pk model, the protonation and deprotonation of terminal surface hydroxyl groups are shown as follows.

$$[MOH^+_2] \xrightleftharpoons{\quad K \quad} [MOH] + [H_s^+] \tag{1}$$

$$[MOH] \xrightleftharpoons{\quad K \quad} [MO^-] + [H_s^+] \tag{2}$$
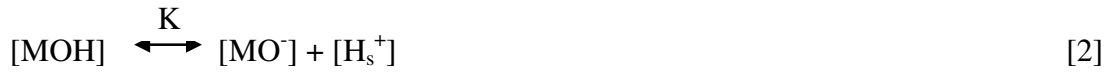
$$K_1 = \frac{[MOH]\,[H_s^+]}{[MOH^+_2]} \tag{3}$$

$$K_2 = \frac{[MO^-][H_s^+]}{[MOH]} \tag{4}$$

$[MOH^+_2]$, $[MOH]$ and $[MO^-]$ are the concentration of protonated, neutral and deprotonated, respectively. $[H_s^+]$ is the proton surface concentration. K_1 and K_2 are the surface ionization constant. These equilibrium constants are ofened expressed in logarithmic form as pk1 and pk2, where $pki = -\log K_i$. The difference between the two surface ionization constant is usually in the term of their logarithm difference (dpk = pk2-pk1).

At the PZC, the concentration of positively charged sites is equal to negatively charged sites. The relationship between the PZC and the pks is

$$PZC = (pk1+pk2)/2 \tag{5}$$

Thus,

$$pk1 = PZC - (0.5*dpk) \tag{6}$$

$$pk2 = PZC + (0.5*dpk) \tag{7}$$

The charging parameters can then be specified as either K_1 and K_2 (or pk1 and pk2) or PZC and dpK.

The Boltzman distribution gives the proton concentration at the surface

$$[H^+_s] = [H^+]\exp\{-e\Psi_o/2k_bT\} \tag{8}$$

where   e = the electron charge

k_b = the Boltzman constant

T = temperature

Ψ_o = the surface potential

The surface charge (σ_o) is defined from the surface site balance by the difference of positively charged site and negatively charged site divided by the total number of sites.

$$\frac{\sigma_o}{F\Gamma_t} = \frac{[MOH^+_2] - [MO^-]}{[MOH^+_2] + [MOH] + [MO^-]} \tag{9}$$

Put [2.3], [2.4] and [2.8] in [2.9] and rearrange the equation

$$\frac{\sigma_o}{F\Gamma_t} = \frac{\{[H^+]\exp(-y_o)/K_1\} - \{K_2\exp(y_o)/[H^+]\}}{\{[H^+]\exp(-y_o)/K_1\} + 1 + \{K_2\exp(y_o)/[H^+]\}} \tag{10}$$

$$y_o = e\Psi_o/2k_bT \tag{11}$$

where F is the Faraday constant and Γ is the surface site density (moles/m^2) and

$\Gamma_t = 10^{-5}Ns/6.02$, where Ns = the site density in sites/nm^2.

James and Healy model is the original base model [13], but in this study, the surface potential non-Nernstian. In a diffuse double layer, the Gouy-Chapman equation relates the relationship between the surface charge and the surface potential

$$\sigma_o = \{8_x10^{-5}\varepsilon\varepsilon_o k_bTN_aI\}^{0.5}\sinh\{ze\Psi_o/k_bT\} \tag{12}$$

where I = ionic strength of solution

ε = relative dielectric constant of the bulk aqueous medium at room temperature

ε_o = dielectric constant of the free space

z = charge of the adsorbing ion

I = total ionic strength of the electrolytes in solution.

N_a = Avogadro's number.

In potentiometric titration studies, proton balance between the surface and bulk liquid is

$$\sigma_o = \frac{F}{ws} (\{ [H^+]_o - [OH^-]_o\} + \{ 10^{-(14-pH)} - 10^{pH}\}) \frac{c^o}{\gamma} \qquad [13]$$

note that ws=SL (surface loading), $[H^+]_o$, $[OH^-]_o$ are initial concentration of proton and hydroxyl

and γ is the activity coefficient from the extended Debye-Huckel equation [18]

$$\gamma = 10^{-0.510(\sqrt{I}/ \sqrt{I+1})} \qquad [14]$$

and

$$I = 0.5 \{10^{-pHi}+10^{(pHi-14)}+10^{-pH}+10^{(pH-14)}\} \qquad [15]$$

where pHi , pH are pH initial and pH final, respectively.

Three unknowns, surface charge (σ_o) , surface potential (Ψ_o) and equilibrium pH (pH) are solved by [2.10], [2.12] and [2.13] using Newton-Raphson method given the point of zero charge (PZC), difference of surface ionization constant (dpk), site density (Ns) and pH initial.

- Adsorption model

The simplified Revised Physical adsorption model has been studied from our group on several papers [1, 5, 8, 16]. Chloroplatinic acid (CPA) and platinum tetraammine (PTA) are often used to adsorb on the oxide support.

 A Langmuir isotherm is used to describe the metal uptake from given pH, K and C

$$\Gamma = \Gamma_{max} \{ KC/(1+KC)\} \qquad [16]$$

Where

K = adsorption equilibrium constant

C = metal concentration

Γ_{max} = maximum adsorption density

The adsorption equilibrium can be calculated by overall Gibbs free energy

$$K = \exp(-\Delta G_{ads})/RT \qquad [17]$$

which ΔG_{ads} (free energy of adsorption) = $\Delta G_{coulombic}$

and,

$$K = \exp(-\Delta G_{coulombic})/RT \qquad [18]$$

The maximum platinum uptake of both complexes are determined to be a close packed monolayer of complexes retaining one (CPA) or two (PTA) hydration sheaths.

$$\Gamma_{max} = \{1/ N_a\pi(x)^2\} \qquad [19]$$

where $x = r_i + 2nhsr_w$, nhs is number of hydration sheaths, N_a is Avogadro's number

r_w is radius of water (1.35 A°), r_i is radius of complex ion; in this model use

r_{cpa} = Radius of CPA (2.95 A°) corresponding to Γ_{max} = 1.6 μmol/m^2 with one hydration sheath

r_{pta} = Radius of PTA (2.41 A°) corresponding to Γ_{max} = 0.86 μmol/m^2 with two hydration sheaths.

The coulombic energy term is calculated by

$$\Delta G_{coulombic} = ZF\Psi_x \qquad [20]$$

where Z is the charge of adsorbed species and Ψ_x is the potential in the plane of adsorption at a position x away from the surface, calculated by assuming in a simple electric double layer and all adsorbed species deposit on one plane given by James and Healy[13]

$$\Psi_x = \left(\frac{2RT}{ZF}\right) \ln \left(\frac{(\exp(ZF\Psi_o/2RT)+1)+(\exp(ZF\Psi_o/2RT)-1)e^{-\kappa x}}{(\exp(ZF\Psi_o/2RT)+1)-(\exp(ZF\Psi_o/2RT)-1)e^{-\kappa x}}\right) \qquad [21]$$

From Debye-Huckel reciprocal double layer length, κ is a function of ionic strength

$$\kappa = 3.31_x10^9\sqrt{I} \qquad [22]$$

Table S1. *Summary Table of typical parameters used in the RPA model*

Parameter	Abbreviation	Value
<u>Support surface</u>		
Point of zero charge	PZC[-]	2 - 9
Surface ionization constant	pk2-pk1=dpk [-]	1-10
Site density	N_s [OH/nm^2]	0.5-10
<u>Precursor</u>		
Radius of complex	r_i [A]	2.95 (CPA), 2.41(PTA)
Number of hydration sheaths	nhs [-]	1 (CPA), 2 (PTA)
Valence	z [-]	-2 (CPA), +2 (PTA)
<u>Solution</u>		
Metal initial concentration	$C_{Pt,in}$ [mol/l]	0.0004-0.012
Surface loading	SL [m$_2$/l]	500 – 200,000
Temperature	T [K]	298.15
pH initial	pHi	0.5-13.5