Non-purged voltammetry explored with AGNES

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Supporting Information

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13 Table SI-1. Computed experimental and theoretical pH^S and estimated *g* factors and metal surface concentrations for
14 various Zn^{2+} and Cd^{2+} solutions in presence of different ligands and buffers. 10% of uncertainty has been considered
15 in all the performed measurements in order to compute the pH range.
16 [a] Visual MINTEQ predicts formation of insoluble metal hydroxides

M^{2+}	$c_{T,M}$/ µM	$c_{T,buffer}$/ M	$c_{T,ligand}$/ µM	pH*	*g*	$[M^{2+}]^S$/ nM	AGNES pH^S	Model pH^S
Zn	1.5	No buffer	No ligand	2.1	1.15	1300	2.1 to 8.2	2.1
Zn	1.5	No buffer	No ligand	4.9	2710	0.551	10.2 to 10.3	10.4
Zn	1.5	[MES]=0.01	[NTA]=1.5	5.0	2.16	322	5.8 to 6.0	5.9
Zn	1.5	[MES]=0.01	[NTA]=1.5	5.5	1.89	237	6.0 to 6.2	6.2
Zn	1.5	[MES]=0.01	[NTA]=1.5	6.0	3.74	75.2	7.1 to 7.3	6.7
Zn	1.5	[MES]=0.01	[NTA]=1.5	6.4	4.53	37.1	7.4 to 7.6	7.9
Zn	1.0	[MOPS]=0.01	[glycine]=200	7.6	7.18	112	8.7 to 8.9	8.8
Cd	1.5	No buffer	No ligand	2.2	1.07	1350	2.2 to 9.3	2.2
Cd	1.5	No buffer	No ligand	4.1	4.15	347	10.0 to 10.2[a]	9.8
Cd	1.5	No buffer	No ligand	5.1	6.90	207	10.2 to 10.3[a]	10.3[a]
Cd	1.0	No buffer	No ligand	6.6	15.1	69.0	10.4 to 10.6[a]	10.3[a]
Cd	2.5	[MES]=0.01	[NTA]=1.5	5.0	1.50	1310	5.7 to 6.2	5.8
Cd	2.5	[MES]=0.01	[NTA]=1.5	6.0	1.24	1080	6.3 to 8.4	6.4
Cd	2.5	[MES]=0.01	[NTA]=1.5	6.6	1.23	900	7.7 to 9.5	7.8

17 Table SI-2. Experimental *g* factors in different calibrations and speciation experiments performed
18 with AGNES under non-purged conditions.
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M^{2+}	Experiment	$c_{T,M}$/ µM	$c_{T,buffer}$/ M	$c_{T,ligand}$/ µM	pH*	20 *g*
Cd	Calibration	From 0 to 0.3	No buffer	No ligand	6.0	20.0
Cd	Speciation	0.3	No buffer	[NTA]=0.13	6.0	25.7
Cd	Speciation	0.3	No buffer	[NTA]=0.20	6.0	35.0
Cd	Calibration	From 0 to 1.0	[MES]=0.01	No ligand	6.7	1.30
Cd	Speciation	1.0	[MES]=0.01	[NTA]=0.19	6.7	1.32
Cd	Speciation	1.0	[MES]=0.01	[NTA]=0.43	6.7	1.39
Cd	Speciation	1.0	[MES]=0.01	[NTA]=0.62	6.7	1.40
Zn	Calibration	From 0 to 1.0	[MOPS]=0.01	No ligand	7.6	5.97
Zn	Speciation	1.0	[MOPS]=0.01	[glycine]=200	7.6	7.18
Zn	Speciation	1.0	[MOPS]=0.01	[glycine]=500	7.6	7.39
Zn	Speciation	1.0	[MOPS]=0.01	[glycine]=750	7.6	7.73

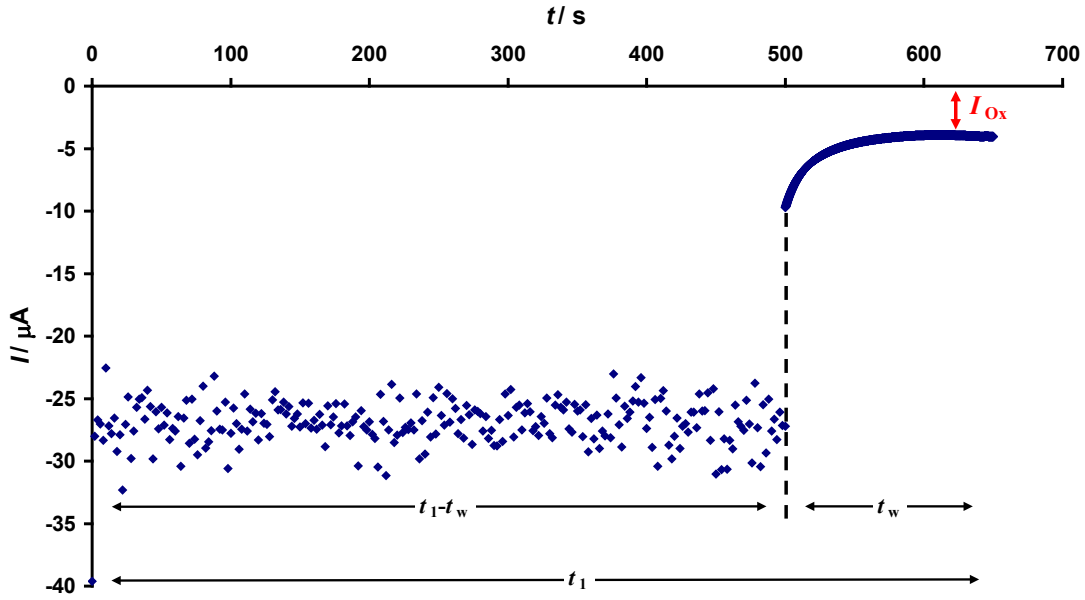

Figure SI-1 Currents measured during the deposition stage: with stirring (t_1-t_w) and without stirring or waiting stage (t_w) in an AGNES experiment for a 1 µM Zn solution, showing how the oxidants current I_{0x} can be obtained at the end of the t_w step.

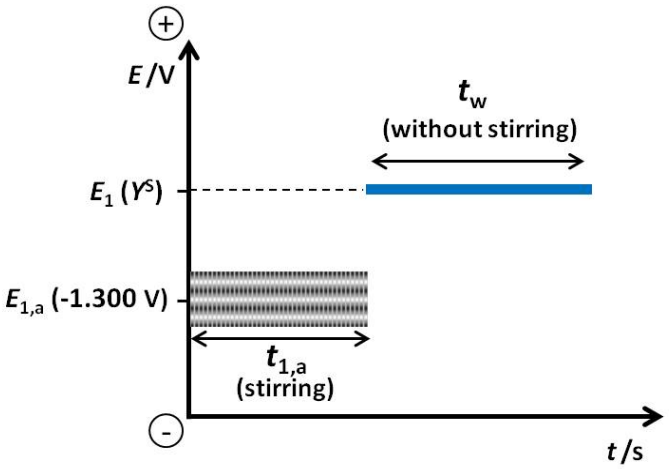

Figure SI-2: Outline of the potential and stirring 2-Pulse program applied in the strategy of splitting the deposition stage into two potential steps with SPE in non-purged solutions. $E_{1,a}$ (applied for a time $t_{1,a}$) is a deposition potential under diffusion limited conditions for accumulation. E_1 (during t_w without stirring) is the deposition potential controlling the gain Y^S.

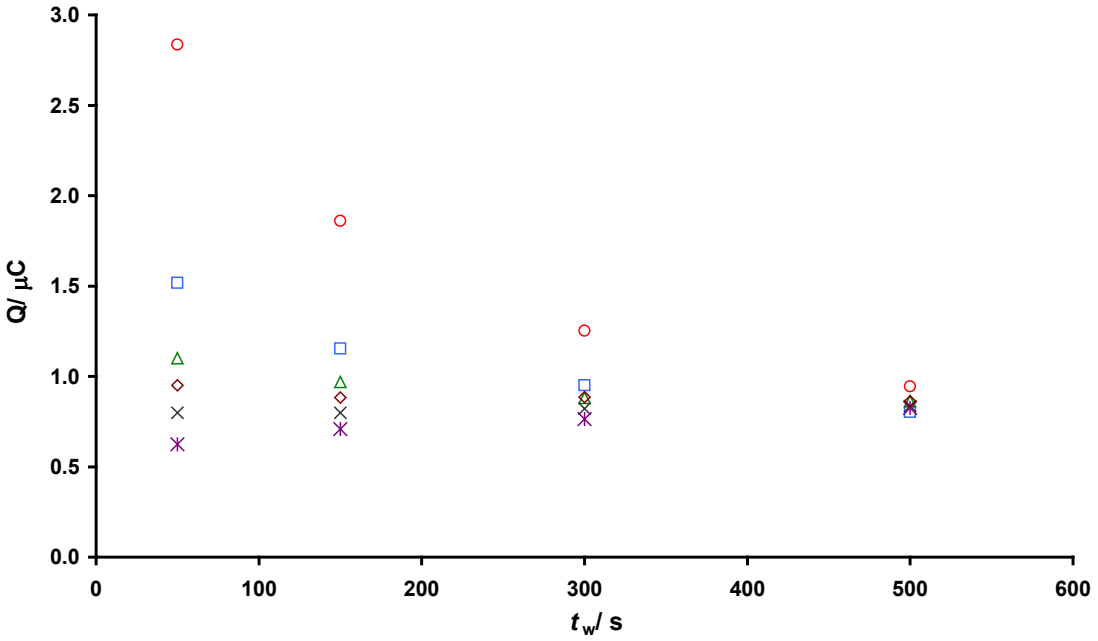

Figure SI-3: Search of the optimal deposition time under diffusion limited conditions ($t_{1,a}$) in a 2-Pulses AGNES procedure without purging in a sample with $c_{T,Zn}$=0.75 µM at pH*= 4.35. AGNES conditions were $E_{1,a}$=-1.300 V, $t_{1,a}$ = 10 s (*), 20 s (×), 25 s (◊), 30 s (Δ), 60 s (□) and 120 s (○), E_1= -1.180 V and t_w between 50 and 500 s. An optimal $t_{1,a}$=25 s has been found.

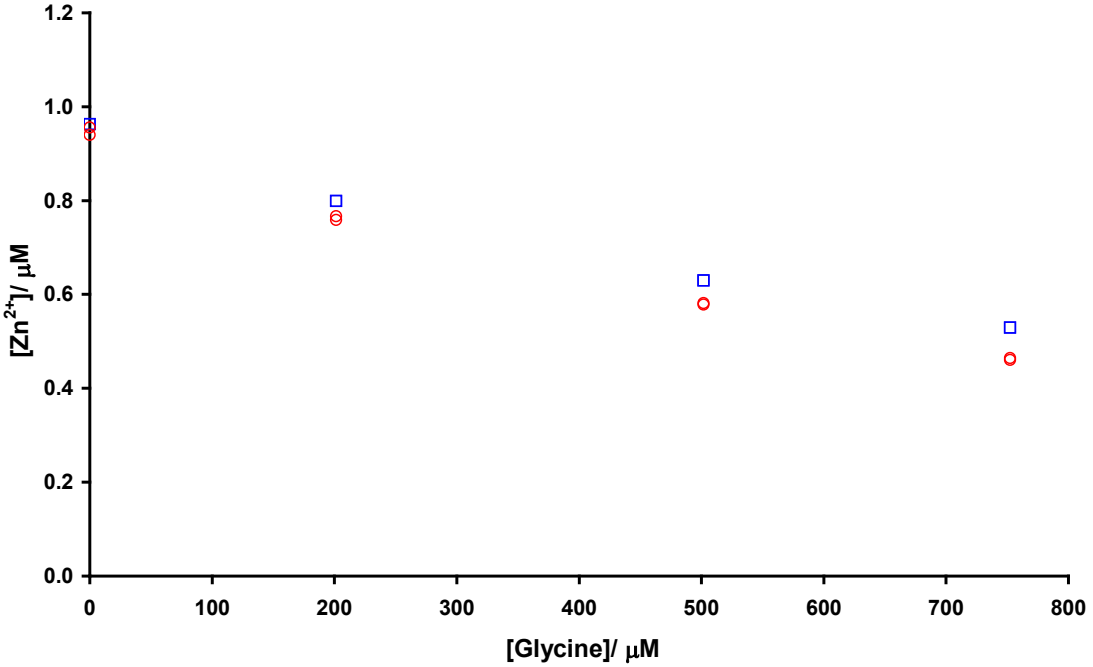

Figure SI-4: Free Zn^{2+} concentration in a titration of a solution $c_{T,Zn}$=1.0 µM with increasing amounts of glycine without purging. [MOPS] = 0.01 M; pH*= 7.6. Parameters E_1=-1.110 V and t_1=650-1150 s and t_w =150 s. Blue squares indicate the value predicted by Visual Minteq and red circles stand for AGNES results.