

# METAL-ION ADSORPTION ON SURFACE MODIFIED MAGNETIC BEADS

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## INTRODUCTION

Interests in our laboratory have focused recently on exploring various aspects of the interactions between solution phase metal ions and self-assembled monolayers (SAM) bearing acid-base functionalities.<sup>1,2</sup> Much of the activity has centered on the use of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) as a highly sensitive and rather specific probe of metal-ion adsorption. As has been reported in a recent publication,<sup>2</sup> the binding of  $\text{Cd}^{2+}$  and  $\text{Fe}^{2+}$  to carboxylate and sulfonate moieties, respectively, brings about significant changes in certain spectral features of these functional groups, providing, thereby, a useful means for monitoring and quantifying metal ion uptake by the monolayer. This work describes the use of the rotating disk electrode (RDE) technique to the study of metal-ion binding on SAM bearing carboxylate groups attached to the surface of iron oxide particles dispersed in the bulk electrolyte, as a function of pH. As will be shown, the RDE provides an expedient means of detecting the amount of  $\text{Cd}^{2+}$  remaining in solution, from which the extent of metal binding to the monolayer can be determined in a rather straightforward fashion.

## EXPERIMENTAL SECTION

Dynamic polarization measurements were performed in 50 mL of  $\text{N}_2$ -purged 25  $\mu\text{M}$   $\text{Cd}(\text{ClO}_4)_2$  (Alfa, 99%) in 0.1M  $\text{NaClO}_4$  (Aldrich, 99%) solutions prepared with ultrapure water using a Pine RDE 3 rotator equipped with a glassy carbon (GC) RDE (disk area: 0.164  $\text{cm}^2$ ) at rotation rates in the range of 400 - 2500 rpm, over the potential range in which Cd electrodeposition ensues. The pH of solution, as measured with a Chemcadet pH meter, was adjusted in the range 3 to 8.4 by adding  $\text{NaOH}$  or  $\text{HClO}_4$  to the main solution. After this set of measurements was completed 1 mL of an aqueous suspension of carboxyl-terminated magnetic iron oxide particles (Sigma, 240  $\mu\text{mol}$   $-\text{COOH}$  per gram, 20 mg/mL), which corresponds to ca. 4.8  $\mu\text{mol}$   $-\text{COOH}$ , was centrifuged, the solid collected and then added to the main solution in the cell to perform an otherwise identical series of electrochemical measurements as those described above in the absence of particles as a function of pH. The effects of the particles on the electrochemistry, including the hydrodynamic flow and possible interactions between the particles and the electrode surface were examined by comparing the results of dynamic polarization experiments in 0.1 mM solutions of  $\text{K}_3\text{Fe}(\text{CN})_6$  (Aldrich, 99%) in 0.1 M  $\text{KCl}$ . The electroactive species in this case is charged negatively and, therefore, would not be expected to adsorb on the negatively charged surface of the magnetic particles. As evidenced by the results obtained (not shown in this work), the particles were found to have no effect of the both the shapes and magnitudes of the recorded currents as a function of the applied potential.

## RESULTS AND DISCUSSION

Shown in Figure 1 are dynamic polarization curves for a solution 25  $\mu\text{M}$   $\text{Cd}(\text{ClO}_4)_2$  in 0.1M  $\text{NaClO}_4$  at pH 7.8 before (Panel A) and after (Panel B) addition of 20 mg of magnetic particles prepared as indicated in the Experimental Section. Data were recorded at a scan rate of 5 mV/s in the range 0.0 to  $-1.0$  V vs. SCE at four rotation rates ( $\omega$ ). In both cases, a plot of the limiting current,  $i_{\text{lim}}$  vs.  $\omega^{1/2}$  yielded straight lines, from which the fraction of  $\text{Cd}^{2+}$  adsorbed by the particles could be determined from the ratio of the slopes yielding a value of 64%. Similar measurements performed at different values of the pH made it possible to construct plots of the percent uptake of  $\text{Cd}^{2+}$  as a function of pH (see Figure 2). As indicated therein, the limiting currents for  $\text{Cd}^{2+}$  electrodeposition in the absence of particles are independent of pH for values above 4.5. This behavior is in stark contrast with that observed in the presence of the particles for which detectable  $\text{Cd}^{2+}$  adsorption was found to occur at a pH of 5.5 yielding at pH = 8.4 a metal uptake of ca. 93%. Efforts are underway to extend these studies to a larger variety of metal ions and thus gain a better understanding of the factors that control these interesting effects.

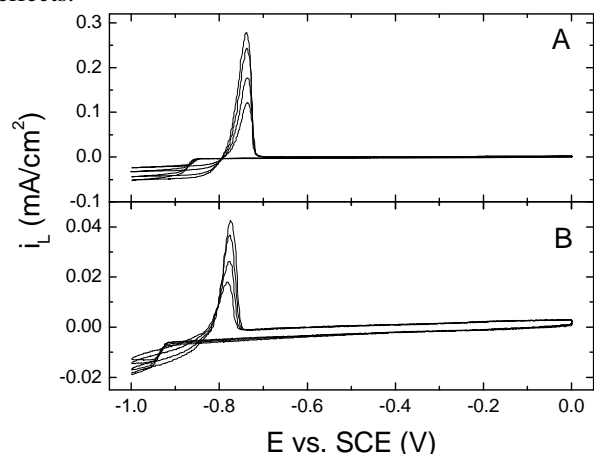


Figure 1. Dynamic polarization curves for 25  $\mu\text{M}$   $\text{Cd}(\text{ClO}_4)_2$  in 0.1M  $\text{NaClO}_4$  at pH = 7.8 before (Panel A) and after (Panel B) addition of 20 mg of carboxylic SAM coated magnetic particles. Scan rate: 5 mV/s; Rotation rates 100, 400, 900, 1600, 2500 rpm.

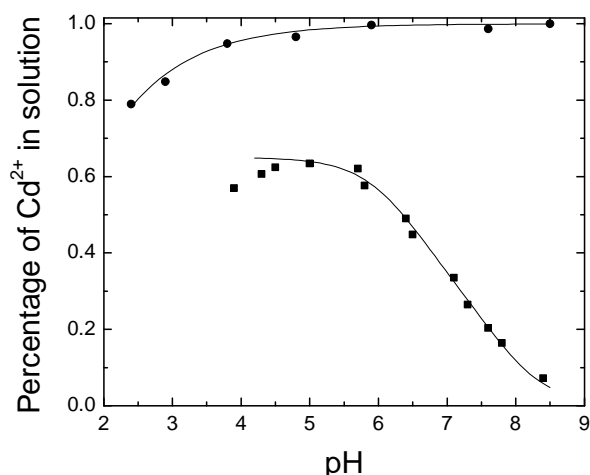


Figure 2. Plots of the percent of  $\text{Cd}^{2+}$  in solution as a function of pH: ● without particles; ■ with particles. Best least-square fits are shown as solid lines.

## REFERENCES

1. Stefan, I.C.; Scherson, D.A. *Langmuir*, **16** (2000) 5945.
2. Stefan, I.C.; Mandler, D.; Scherson, D.A. *Langmuir*, **18** (2002) 6976.