

## Electrochemical Examination of Cobalt Redox Chemistry in Thin Films

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In this work, electrochemical techniques are employed to examine the redox catalysis of ligand substitution with Co(II)/Co(III) in a thin film format, one that is suitable for use as a multi-layer analytical device. The cobalt ligand substitution chemistry of these films has been explored in an intensive manner at Kodak as a means of signal amplification in imaging and sensing systems.(1) In addition, this general category of catalysis has been described in treatises on inorganic chemistry and has been the subject of electrochemical studies of analogous chromium systems.(2)

The general scheme for the reaction sequence is given in Figure 1. An inorganic complex that is kinetically inert to substitution is reduced in an electron transfer step. This initiates a ligand exchange from the more labile reduced complex  $[RL_i]^-$  with a second ligand  $L_{ii}$ , which is present in great excess. The catalysis propagates through a reduction of another  $RL_i$  species by the  $[RL_{ii}]^-$ . This catalysis can cycle until electron traps intercept the  $[RL_{ii}]^-$  species and terminate the reaction.

This general chemistry was examined in the case of Co(II)/Co(III) complexes (1) to provide an alternative to the silver amplification process in silver halide photography. The solution chemistry was transferred to thin layer coatings and imaging systems were developed that required excitation of a quinone in the photogeneration of an electron which initiates the reaction. Amplification factors of 100-1000 fold were observed. Kodak has also patented the use of the cobalt chemistry for wet analytical processes. However, thin layer technology for this process was not developed because of numerous difficulties encountered with the analogous imaging system.

We have assembled a thin layer analytical system for the use of cobalt amplification chemistry in sensing. In one example of this system, we have used Co(III)(NH<sub>3</sub>)<sub>6</sub> as the kinetically inert  $RL_i$  complex and 1-(pyridyl-azo)-2-naphthol (PAN) as the ligand  $L_{ii}$ . The source of the reducing power is Co(II)(cyclohexylsalicylaldimine)<sub>2</sub> (Co(II)CHSA). The spectra of the PAN, the Co(II)(PAN)<sub>2</sub> and Co(III)(PAN)<sub>2</sub> complexes in Figure 2 show that as the reaction proceeds in solution, the absorption of the solution shifts from 450 nm out to 600 nm, going from orange to black.

Electrochemical analysis of this system using second harmonic voltammetry in acetone has shown that the thermodynamics of the process are somewhat different than expected. The reducing power of the Co(II) is obtained through a ligand exchange of the Co(II)CHSA complex with PAN to produce Co(II)(PAN)<sub>2</sub>. The subsequent electron transfer from Co(II)(PAN)<sub>2</sub> to Co(III)(NH<sub>3</sub>)<sub>6</sub> is thermodynamically uphill, with the overall process being driven by the irreversible loss of

NH<sub>3</sub> from the liganding sphere of Co(II).

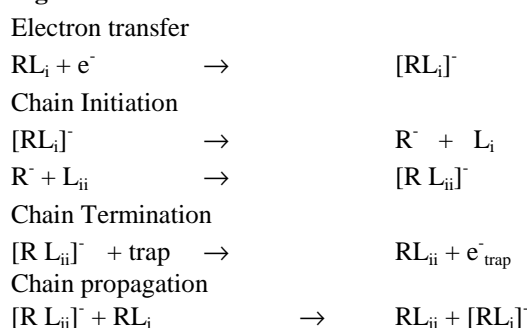
To insert these processes into a multi-layer analytical element using polymers as binders is a formidable task. A significant part of this problem is found in the change in electrochemistry of the system upon introduction of this solution chemistry into the thin layer system.

We report on the use of microelectrodes to study these electrochemical process in thin layer polymer films and have found that the thermodynamics and kinetics are altered. The hydrophobicity and pH characteristics of the polymer have been found to affect the complexation constants of the cobalt. The diffusion constants of the reactions are found to drop significantly. Full complexation of the Co(II) by PAN is hindered in many films.

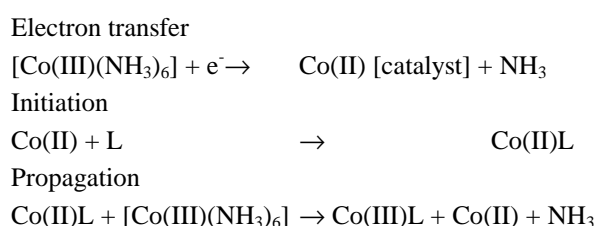
### References

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### Figure 1 General Scheme



### Figure 2 Amplification with Cobalt Chemistry



### Figure 3 Absorption Spectra

