

Electrostatic Binding of Metal Complexes to Electrode Surfaces Coated with Highly Charged Polymeric Films

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Under pressing conditions (high concentrations of incorporated ion, low concentration of supporting electrolyte, long exposure times) it is possible to incorporate greater quantities of ferricyanide into protonated PVP films than would correspond to electrostatic neutralization of all of the positive charge present on the fully protonated pyridine groups. For example, a PVP film containing 4.6×10^{-7} moles cm^{-2} of pyridine incorporated as much as 2×10^{-7} moles cm^{-2} of ferricyanide. We presume that under these conditions the $\text{Fe}(\text{CN})_6^{3-}$ is incorporated in the form of an ion pair with a cation of the supporting electrolyte. With IrCl_6^{2-} the maximum quantity incorporated into films never exceeded ca. 30% of the total possible cationic charge in the polyionic film.

Multiply-charged cationic complexes can also be incorporated electrostatically into polyanionic films. For example, Figure 3 shows voltammograms

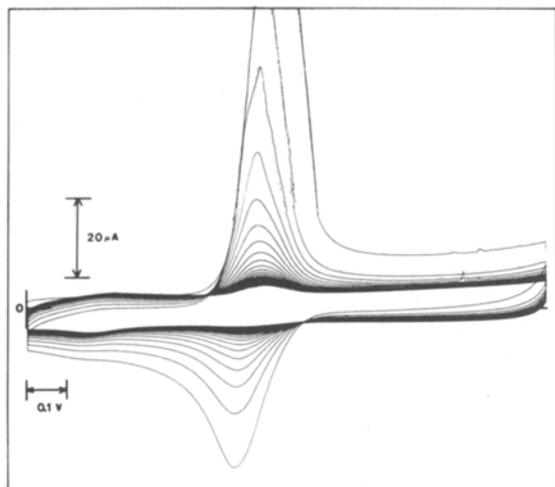


Figure 3: Cyclic voltammograms for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ attached to a pyrolytic graphite electrode coated with ca. 4×10^{-7} moles cm^{-2} of carboxylic acid as polyacrylic acid (M.W. = 2.2×10^5). The coated electrode was soaked for 5 min. in 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ at pH 6.1, washed for 10-20 s. with water, transferred to supporting electrolyte (0.2 M CF_3COONa + 5 mM $\text{Na}_2\text{B}_4\text{O}_7$; pH 8.1) and the potential cycled continuously between +0.3 and -1.0 volt at 200 mV s^{-1} . The time elapsed between the first and last scans was ca. 7 min.

for an electrode that was coated with polyacrylic acid, soaked in a 1 mM solution of $\text{Ru}(\text{NH}_3)_6^{3+}$ at pH 6.1 (where the polymer is converted to a polyanion) and transferred to pure supporting electrolyte solution. Large quantities of the tripositive cation are clearly incorporated into the polyanionic film (ca. 10^{-8} moles cm^{-2} of $\text{Ru}(\text{NH}_3)_6^{3+}$) but repetitive cycling of the potential leads to continuous departure of the $\text{Ru}(\text{NH}_3)_6^{3+}$ from the film. The loss of $\text{Ru}(\text{NH}_3)_6^{3+}$ occurs whether or not the potential is cycled but the rate of loss is greater during cycling when the charge on the incorporated cation is diminished by one unit during each half-cycle. The less permanent binding of $\text{Ru}(\text{NH}_3)_6^{3+}$ by the polycarboxylate coating may be associated with the more hydrophilic nature of this film compared with PVP: The latter polymer is insoluble in aqueous acid while poly-sodium acrylate is water soluble (although films deposited on pyrolytic graphite resist dissolution). The activation barriers for entry or departure of cationic reactants from the polycarboxylate layer are apparently considerably smaller than for PVP.

The attractive simplicity of the electrostatic binding procedure for holding large quantities of metal complexes on electrode surfaces is complemented by the variety of ionic polymers that are available to serve as anchoring matrices. In addition, the procedure allows complexes to be introduced on electrode surfaces without change in their primary coordination sphere, a factor that could be of considerable importance with catalytically active complexes. These attributes have encouraged us to explore more broadly the combinations of charged complexes and ionic polymers that may be exploited to produce electrode surfaces laden with desired ionic reactants.

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