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Electrochromic Cells Using Some Transition Metal  
Complexes

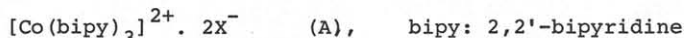
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Electrochromism has attracted increasing interest in the last few years for its potentially broad application in display media. Recently several new electrochromic (EC) systems have been reported which are based on some electrochemical effects.<sup>1-4)</sup> In such systems organic compounds and transition metal oxides are mostly common, whereas no attempts have been published on EC cells using transition metal complexes of organic ligands.

In this paper we wish to report the preliminary results of the EC cells using Co(II) complex salts of the general formula:



The electrochemical behavior of Cobalt 2,2'-bipyridine complexes has been the subject of extensive study.<sup>5-7)</sup> The complex cation  $[\text{Co}(\text{bipy})_3]^{2+}$  is reduced at cathode in a one-electron step to  $[\text{Co}(\text{bipy})_3]^{1+}$  which exhibits deep blue color. The redox potential  $E_0$  in aqueous media is ca. -1.2V vs SCE. The polarogram of the aqueous solution of (A) where  $\text{X}^- = \text{NO}_3^-$  is shown in Fig. 1. The complex cation  $[\text{Co}(\text{bipy})_3]^{1+}$ , pairing with  $\text{X}^-$ , immediately forms a salt  $[\text{Co}(\text{bipy})_3]^{1+} \cdot \text{X}^-$  (B). (B) is insoluble in water and deposits onto the cathode to form a deep blue film. Since the above electrochemical reaction is reversible,<sup>5)</sup> by inverting the electrode polarity the colored film of (B) is reversely oxidised. The resultant (A), which is soluble in water, diffuses away into the solution.

The cross section of our experimental EC cell is illustrated in Fig. 2. A typical composition of the EC system is shown in Table 1. The solution is opacified by the addition of  $\text{TiO}_2$  powder to hide the coloration at the back electrode. The light reflectance was measured using a tungsten lamp as shown in Fig. 3. The result is given in Fig. 4 as a function of electrical charge flowed between the electrodes. The color persisted more than 30 minutes after the removal of writing voltage when oxygen was excluded from the cell. This limited persistence is explained by assuming the reaction between Co(I) and Co(III). Co(III) is formed at anode when Co(I) film is not present on the anode. This formation of Co(III) is important against irreversible electrochemical degradation. More detailed reaction scheme will be mentioned.

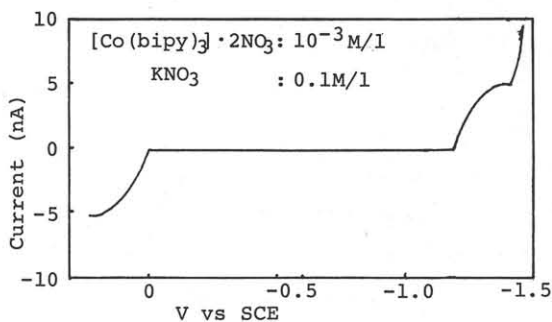


Fig. 1. D.c. polarogram of aqueous solution of  $[\text{Co}(\text{bipy})_3] \cdot 2\text{NO}_3$ . Supporting electrolyte:  $\text{KNO}_3$ .

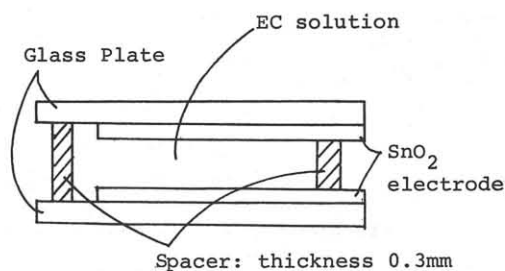


Fig. 2. Cross section of the experimental EC cell

Table 1. Typical composition of the EC cell

compounds	concentration
$[\text{Co}(\text{bipy})_3] \cdot 2\text{NO}_3$	$7.0 \times 10^{-3} \text{ M/l}$
$\text{KNO}_3$	50 mM/l
$\text{TiO}_2$	—

solvent:  $\text{H}_2\text{O}$

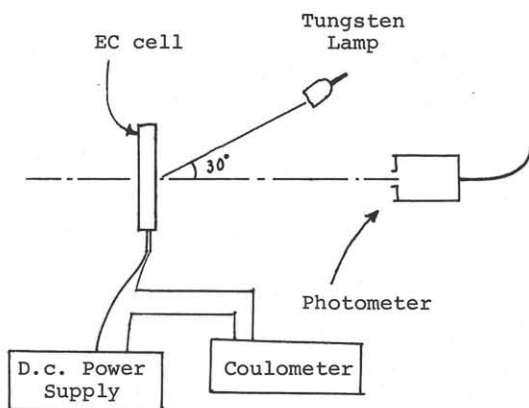


Fig. 3. Configuration of light reflectance measurement

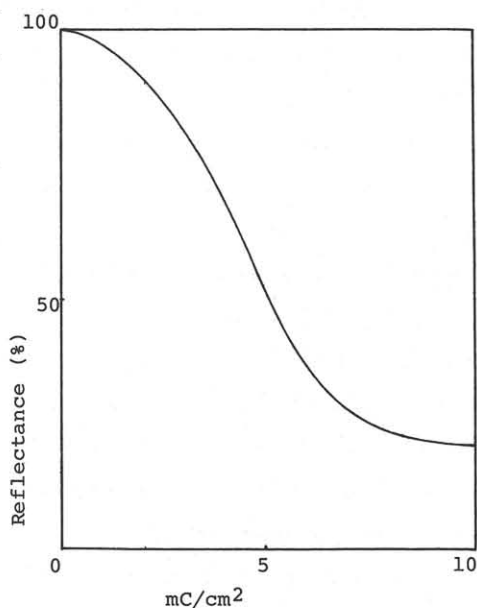


Fig. 4. Light reflectance as a function of charge density. Applied volt.: 1.7 V

#### References

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