

Use of an optical fiber attachment for spectro-electrochemical studies

Application Note

Author

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Introduction

The reduction of carbon dioxide is catalyzed by a number of metalloporphyrins, phthalocyanines and related compounds. Cobalt(II) phthalocyanine (CoPc) has been identified as one of the more active materials. The mechanism of the reaction remains unclear, although it is generally believed that the initial step is the electrochemical reduction of the cobalt(II) ion to cobalt(I).

Spectro-electrochemistry is a powerful method to study the reduction of CoPc and the reaction of this with CO₂. In conventional spectro electrochemical studies an OTTLE (Optically Transparent Thin Layer Electrochemical) cell is utilized. The advantages of such cells, including small sample volume and rapid electrolysis, in fundamental studies are well documented. The restricted dimensions of an OTTLE cell make it virtually impossible to introduce a reactant to the system after electrolysis and place considerable constraints on the electrode materials which can be utilized, and as such they are less than ideal for studies in electro-catalysis.

In the present work we have utilized an optical fiber probe to study the reduction of CoPc in DMF and the reaction of the species thus formed with CO₂. There are a number of advantages in using an optical fiber probe for this work, most importantly the ability to utilize a conventional electrochemical cell, which is too bulky to fit within the sample compartment of the instrument, so as to enable CO₂ to be admitted to the solution. Further, since no electrode material is within the optical beam it was possible to utilize a mercury pool electrode.



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Experimental

UV-Vis spectra were recorded using a Cary 5E spectrometer equipped with a Fiber Optic multiplexer. A UV-Vis optical fiber probe was supplied by C-Technologies. All electrochemical reactions were carried out in a mercury pool bulk electrolysis cell using a PAR 173 potentiostat. The platinum counter and calomel reference electrodes were separated from the bulk solution with Vicor Frits. The supporting electrolyte was 0.1 M tetrabutyl ammonium tetrafluoroborate (TBABF₄). The experimental arrangement is shown in Figure 1.

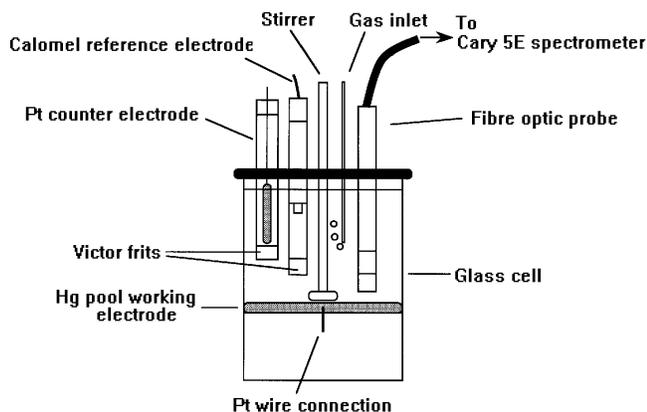


Figure 1. Design of the electrochemical cell used for spectroelectrochemical experiments with a fiber optic probe

Results

The spectral changes between 350 and 820 nm which accompany the 1 electron reduction of cobalt(II) phthalocyanine at -1.8 V vs SCE in DMF are shown in Figure 2. There are three well defined isobestic points indicating that only two absorbing species are present in solution. The electronic absorption spectra of the electrochemically formed species is essentially identical with that of a sample of Co(I)Pc prepared by chemical reduction and the various absorption bands can be assigned to $\pi \rightarrow \pi^*$ transitions.

The addition of CO₂ to the electrochemically produced Co(I)Pc solution results in the rapid reformation of Co(II)Pc. Indeed in the presence of CO₂ it was not

possible to stabilize Co(I)Pc even at -1.8 V.

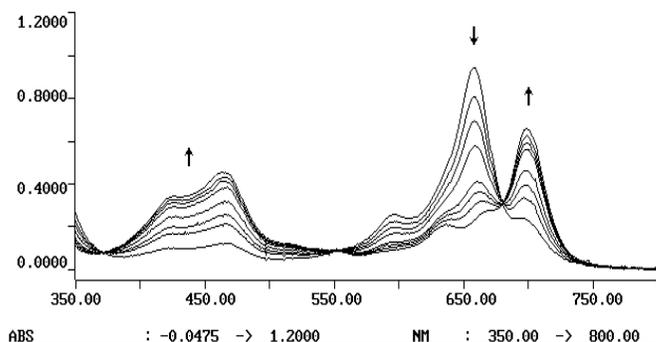


Figure 2. Spectral changes that accompany the one electron reduction of Co(II)Pc in 0.1 M (TBA)BF₄/DMF under an argon atmosphere. Applied potential -1.8 V vs SCE

The presence of well defined isobestic points, Figure 3, suggests that the reduction of CO₂ involves a one electron transfer from Co(I)Pc rather than the formation of more highly reduced species such as Co(I)Pc⁻.

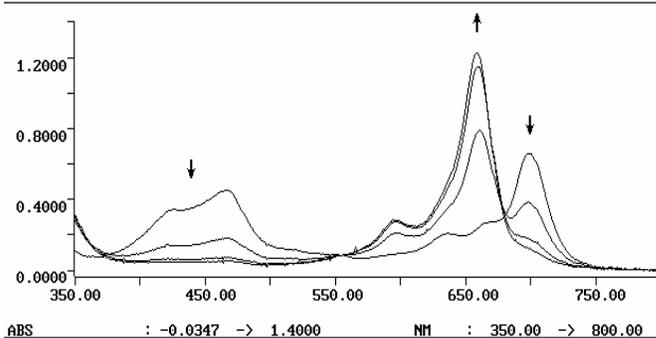


Figure 3. Spectral changes that occur upon the addition of CO₂ to Co(I)Pc in 0.1 M (TBA)BF₄/DMF at a potential of -1.8 V vs SCE

Conclusion

An optical probe has been successfully employed to study the spectral changes which accompany the reduction of Co(Pc) at a Hg electrode. Importantly the probe enables the routine use of Hg electrodes in spectro-electrochemical studies and provides a convenient method to study reactive species without the use of more specialized sampling cells such as an OTTLE cell.

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© Agilent Technologies, Inc., 1993, 2011
Published March, 2011
Publication Number SI-A-1140



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