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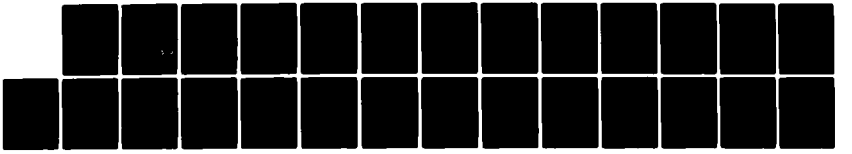

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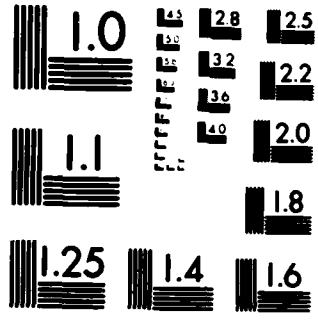

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APPLICATIONS OF IN SITU MOSSBAUER EFFECT SPECTROSCOPY TO THE STUDY OF ELECTRODE-ELECTROLYTE INTERFACES

by

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Mössbauer effect spectroscopy has emerged as a powerful tool in the in situ examination and analysis of the physico-chemical properties of active nuclei containing species either adsorbed at solid-liquid interfaces or present in layers on electrode surfaces. Applications are given for in situ Mossbauer in-emission and transmission modes as well as an illustration of the newly developed in situ electron conversion Mossbauer spectroscopy. Several aspects of the experimental technique are discussed and the literature in the area is reviewed.

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I. INTRODUCTION

Mossbauer spectroscopy has long been recognized as a powerful analytical tool in a number of areas ranging from metallurgy to biological chemistry.[1] The highly monoenergetic character of the recoil free emitted γ-rays provides an extremely sensitive probe of the chemical environment of active nucleides. Among these the non-radioactive ^{57}Fe isotope has been by far the most widely studied, mainly because the high recoilless fraction, the relatively high natural abundance of ^{57}Fe (2.24%) which often allows the use of non-enriched specimens at room temperature, and the occurrence of iron in a wide variety of molecules of inorganic and biochemical interest. In spite of the growing number of applications to diverse fields of research, only a few illustrations have appeared in the literature concerning the utilization of this technique in electrochemistry. The present work will attempt to summarize the present status of Mossbauer spectroscopy as it relates to problems in interfacial electrochemistry, placing special emphasis on the latest developments in in situ measurements.

II. PRIOR STUDIES

Underpotential Deposition

In situ Mossbauer spectroscopy was first applied to the study of underpotential deposition of tin on platinum.[2] This experiment was performed by adsorbing radioactive ^{119}Sn onto a large surface area platinum black electrode ($\sim$ 4000 cm^2) at potentials anodic to that corresponding to bulk deposition. Based on the principles of Mossbauer spectroscopy, only γ-rays emitted by tin bound tightly to the substrate can be resonantly absorbed by an appropriate absorber placed between the electrode (source) and the detector in the emission experiment configuration. The results obtained indicated a close similarity between the Mossbauer spectra of bulk tin and that of a full monolayer of underpotential deposited metal. In particular, the isomer shift value was found to lie between those of bulk tin and Sn-Pt alloy.

Upon a reduction in the total tin coverage the quadrupole splitting was observed to increase with a corresponding decrease in the isomer shift. An increase in the asymmetry of the electric field due to the absence of near tin neighbors at lower coverages with a simultaneous decrease in binding distance between Sn and Pt was suggested as a possible explanation of the experimentally observed results.

Passivation Studies

An approach similar to that used in the underpotential deposition study outlined above was followed by Simmons et al.[3] in their in situ investigation of the passivation and anodic oxidation of Co in borate buffer, pH 8.5. In this case ^{57}Co enriched films of a thickness ranging from 20 to 200 Å were electroplated onto a non-enriched cobalt electrode. At the beginning of the experiments the films were polarized at -1.1 V vs. SCE in order to reduce cobalt oxides formed during the plating and handling. This reduction procedure yielded a six line Mossbauer spectra characteristic of ^{57}Fe in a Co matrix. The values of the isomer shift and internal magnetic field obtained in the case of electrochemically formed thick films (∿200 Å) were different from those corresponding to either hexagonal closed packed or cubic crystalline modifications of the cobalt lattice. These discrepancies were ascribed by these authors to a thickness effect or to the possible presence of H_2, defects and/or impurities in the film. A considerably different spectra was found for cathodically polarized thin films (∿50 Å). In this case the lines were shown to be much broader, and although it was suggested that relaxation or magnetic dilution effects could possibly account for this behavior no firm conclusions were reached.

In-situ Mossbauer measurements were performed at four different potentials comprising active, passive and transpassive regions for Co. Due to the high currents arising from metal dissolution in the active region the specimens were quenched at liquid nitrogen temperature, a procedure which in principle would preserve the electrical state of the interface unaltered.

Upon subtracting the contributions due to the unreacted metal a spectrum exhibiting two sets of quadrupole doublets was obtained for an electrode polarized at -100 mV vs. SCE. One of these (δ_1 -1.31 vs S.S.*; Δ_1 2.83)‡ was assigned to ^{57}Fe in the 2+ oxidation state while the other (δ_2 -0.59 vs. S.S., Δ_2 0.78) to Fe^{3+}. No evidence of iron in the ferrous state was found when the applied potentials were in the passive region (+200 mV to 500 mV) and a single doublet with parameters similar to the ferric species observed at -100 mV was found to give the best statistical fit of the Mossbauer difference spectrum. An additional iron species, (δ 0.14), however, was generated at 800 mV vs. SCE and it was attributed to iron in the +4 oxidation state. As pointed out by these authors, the presence of highly oxidized species in the emission spectra could be due to Auger after effects or chemical effects. The first of these relate to the emission of secondary electrons following the initial electron capture of inner core electrons in the radioactive decay of ^{57}Co. The second effect refers to the different chemical potential of cobalt and iron in the matrix. These phenomena introduce a certain degree of uncertainty in the interpretation of emission spectra although a detailed study of the emission of known species can be useful in the final analysis.

The use of <u>in situ</u> Mossbauer spectroscopy in the transmission mode was first reported by O'Grady and Bockris[4] in an attempt to gain insight into the physicochemical structure of the passive layer on iron. The isomer shift and quadrupole splitting for a passive film formed at pH 6.8 were found to correspond to those of iron polymers containing di-oxy and di-hydroxy bridging bonds between the metal atoms. A comprehensive <u>in situ</u> Mossbauer study of the passive film on iron in borate buffer, pH 8.4, was reported later by O'Grady.[5] An

*Stainless steel standard
‡Isomer shifts and quadrupole splittings are given in mm/sec.

important feature of the electrochemical cell used was the ability to decrease the distance between the working electrode and the window, thus reducing the attenuation of the γ-ray beam due to the electrolyte. This was achieved by placing the working electrode on the front of a hollow movable cylinder supported by the cell body. In order to detect a signal from the very thin passive film, a layer of ^{57}Fe was electroplated onto a vapor deposited gold mylar piece. The electrodeposition was performed inside the same cell to minimize handling and a prolonged exposure to the atmosphere. The bath was later drained and the cell chamber washed several times with borate buffer while the working electrode remained under cathodic protection. The results obtained at room temperature were in agreement with those of O'Grady and Bockris referred to above. Additional insight into the properties of the passive film was provided by the temperature dependence of the Mossbauer spectra. These measurements indicated a sperimagnetic character of the film. This phenomenon is characterized by large values of the isomer shift and quadrupole splitting at room temperature, which disappear below the transition temperature, and a very low magnetic ordering temperature (20-100 K). This effect has been found in amorphous iron(III) oxides and hydroxides. Based on this information, O'Grady concluded that the passive film is amorphous and polymeric rather than highly structured and it consists basically of chains of iron atoms linked by dioxy and dihydroxy bridging bonds which are in turn linked by water to form a continuous layer extending throughout the iron surface.

These studies have been extended by Eldridge *et al.*[6] using O'Grady's cell. The results for iron passive films in borate buffer, pH 8.4 were very similar to those referred to above although a slightly larger value for the quadrupole

splitting was found indicating structural disorder. The isomer shift and quadrupole splitting showed little or no dependence on the particular passivating potential in a region between 1.05 and 1.55 vs. RHE. An increase in the resonant area of the passive film was observed upon repeated potential stepping of the iron electrode between -0.35 V and 0.85 V vs. RHE (p_{H_2} = 1 atm) with a significant drop in the quadrupole splitting. In order to investigate the possibility of ferrous ions being oxidized and precipitated from solution, a natural iron film was passivated in the presence of an appreciable amount of $^{57}Fe^{2+}$ in the borate buffer. The Mossbauer spectra showed only very small iron peaks arising from the iron substrate, leading these authors to conclude that if iron species in solution are incorporated into the film the amount is too small to be detected or alternatively they would form part of a loosely bound overlayer with a negligible recoil-less fraction at room temperature.

Films and Adsorbed Species

Recently Itaya et al.[7] have reported the first in situ Mossbauer study of Prussian blue films formed electrochemically from $^{57}FeCl_3$ and $K_3Fe(CN)_6$ equimolar solutions. These films have been shown to undergo a marked electrochromic effect changing from blue (open circuit) to transparent at potentials ~0.6 V vs. SCE in 1.0 M KCl(pH 4.0). A drastic change in the Mossbauer spectra was observed upon polarization into the transparent region indicating a quantitative ferrous to ferric transition arising solely from the iron incorporated from the labelled species in solution.

The study of molecules adsorbed on electrode surfaces through in-situ Mossbauer spectroscopy was initiated by Scherson et al.[8,9] High surface area carbons were used as a substrate to allow adsorption of an amount of active nuclei containing species sufficient for a signal to be observed in

a conventional transmission experiment without the need of further enrichment. Iron phthalocyanine (FePc) was chosen as a model system because of its importance as a catalyst in the electroreduction of O_2 and the availability of previous ex situ Mossbauer studies.

III. PRESENT STUDIES

FePc Adsorbed on High Surface Area Carbons

a) Ex situ. Iron phthalocyanine (Kodak) was preadsorbed onto the carbon from a pyridine solution ($\sim 10^{-3}$ M), and the solvent later removed by vacuum evaporation. The specimens were subsequently treated at 420°C under a continuous flow of He:H_2 (4:1) at 1 atm. This last procedure was used to remove pyridine from the adduct and to eliminate O_2 bound to the macrocyclic or otherwise trapped in the substrate matrix. Curves A and B in Fig. 1 show the ex situ Mossbauer spectra of ~30% w/w FePc preadsorbed on Pittsburgh Carbon Co. RB carbon ($\sim 1{,}200\ m^2 g^{-1}$) and Vulcan XC-72 ($\sim 250\ m^2 g^{-1}$), respectively. A statistical analysis of the spectra yielded for both samples contributions due to metallic iron (four of the six lines are clearly seen) and two doublets. Similar experiments using pure He during the heat treatment showed no iron in metallic form, clearly indicating that H_2 can reduce the central iron ion at this timperature. The isomer shift, δ, and quadrupole splitting, Δ, of one of the doublets (1) corresponded to bulk FePc while the parameters for the second doublet (2) common to both specimens did not agree with any form of FePc reported in the literature. Based on the fact that the resonant absorption areas of this species relative to that of the bulk material increased appreciably in the case of the very high area RB carbon as compared tothe XC-72 carbon, the corresponding doublet was attributed to FePc bound to the carbon surface. The small value for the quadrupole splitting of doublet 2 was ascribed to an interaction of iron in the macrocyclic with

Lewis basic groups on the carbon surface. This fact was substantiated by a comparison with Mossbauer parameters of a series of axially coordinated FePc adducts.[10] According to these studies an increase in the basicity of the ligand results in a decrease in the magnitude of Δ without changes in δ. Based on this information it can be concluded that FePc is most likely bound with its plane parallel to the carbon surface in the fashion depicted in Fig. 1 (Insert). Contributions from Fe impurities in the RB carbon were not included in the fit to curve A, Fig. 1. No iron species were found in XC-72 carbon without preadsorbed catalyst.

b) In situ. Electrodes for in situ Mossbauer measurements were prepared by mixing the carbon/catalyst powders with a Teflon emulsion following a procedure and using a cell described in detail elsewhere.[8] The cell container was a plastic bag. The arrangement was such that the thin disk-shaped working electrode could be potentiostated to a given potential relative to a reference electrode using a parallel high area carbon counter electrode of similar construction but not containing the FePc. When the current had decayed to a low value, the working electrode was repositioned and the flexible plastic cell walls brought very close to the two opposite sides of the working electrode. The γ rays involved in the Mossbauer radiation were then passed through the working electrode with the electrolyte path length reduced to a low value.

A decrease in the quadrupole splitting for doublet 2 was observed upon immersion of a dry electrode into a 1 M NaOH solution. This phenomenon is attributed to the formation of a hydroxyl axial coordinated FePc adsorbed species. In order to substantiate this, an experiment has been performed by comparing the Mossbauer spectra of an electrode in 1 M NaOH with that of

the same electrode in 0.5 M H_2SO_4. The quadrupole splitting in the latter solution was found to increase to a value intermediate between dry and basic media. This indicates a decrease in the basicity of the axial ligand and is most probably due to a protonation of the hydroxyl group to form water, a much weaker Lewis base than OH^-.

No significant changes in the magnitude of either the isomer shift or the quadrupole splitting were found upon polarization of a ~29% w/w FePc on RB carbon electrode in 1 M NaOH in the region of potential between -0.60 V and +0.20 V vs. $Hg/HgO,OH^-$, with the heat treatment in $He:H_2$ (4:1) and the pyridine removed by evaporation in vacuo. The relative resonant absorption areas of the doublets corresponding to bulk and adsorbed species $A_{bulk}/A_{adsorbed}$, however, was found to decrease at the most anodic potential. Based on the literature values for a bulk Fe(III)Pc species formed by heat treatment in an O_2 atmosphere, the estimated standard electrode potential for the $Fe^{II}Pc/Fe^{III}Pc$ couple, and the quasi-reversible character of Mossbauer spectra, Scherson et al.[8] suggested that the efrect may be due to a ferrous-ferric transition of the bulk material.

Curve A, Figure 2 shows the Mossbauer spectrum of a 15% w/w FePc on XC-72 carbon powder preadsorbed with FePc in the manner described in a), although heat treated under He and with the pyridine removed by evaporation in He at 1 atm. Such a treatment avoids iron reduction and enhances the adsorption process as judged by the disappearance of the characteristic bulk FePc doublet. The caption in Fig. 2 lists the Mossbauer parameters found for these specimens placed as powders (no potential control) in contact with alkaline and acid solutions and then partially dried, which are in qualitative agreement with those obtained using electrodes. These experiments demonstrate the ability of Mossbauer spectroscopy to monitor the axial chemistry of molecules such as FePc adsorbed on electrode surfaces and could

potentially give insight into the mechanistic pathways of certain classes of electrochemical reactions, in particular oxygen reduction.

In Situ Electron Conversion Mossbauer Spectroscopy

The feasibility of in situ electron conversion Mossbauer spectroscopy has been recently demonstrated by Kordesch et al.[11] These authors used a circular iron electrode made by electrodepositing a thin film of ^{57}Fe onto a vacuum evaporated gold film on a Melinex substrate. The disk was mounted on the spindle of a clock motor (1 rpm) and a plastic bag was then placed around the electrode to serve as both the electrochemical cell and the electron counting gas chamber. A conversion electron detector was placed in the path of the γ-ray beam and exposed to the inner part of the chamber through a hole in the plastic bag. Additional orifices in the upper part of the chamber allowed introduction of a reference and an auxiliary electrode. A deaerated borate buffer solution, pH 8.4, was then introduced into the cell to cover only the lower part of the iron disk. The electrode was then polarized into the cathodic protection region (-1100 mV vs. SCE) and the motor activated. Curve A in Fig. 3 shows the in situ electron conversion Mossbauer spectrum obtained, exhibiting the center two of the six lines corresponding to metallic iron. The electrode was then stepped into the passive region (+600 mV vs. SCE) and a period of two hours was allowed before recording the spectrum. Curve B in Fig. 3 gives the spectrum of the passive film. This experiment indicates that potential control of the interface is maintained for an emersed electrode.

Overall, Mossbauer spectroscopy can provide in situ information regardling the structure of a variety of electrode-electrolyte interfaces not accessible in most cases with other spectroscopic methods. Although

the emphasis has been focused on iron, extensions of this technique to a number of other active elements will certainly be developed in the future.

Acknowledgments

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Figure Captions

Figure 1. Ex-situ Mossbauer spectra of ∿30% w/w FePc on high surface area carbon. Specimens prepared by mixing the carbon with an FePc solution in pyridine and subsequently removing the solvent by evaporation under vacuum. Heat treatment: 420°C under He:H_2 (4:1) atmosphere.

A. RB carbon (surface area ∿ 1200 m^2g^{-1})

B. XC-72 carbon (surface area ∿ 250 m^2g^{-1})

Insert: most probable configuration of FePc adsorbed on carbon.

Figure 2. Mossbauer spectra of 15% w/w FePc on XC-72. Specimens prepared as described in caption, Fig. 1. Only doublet 2 is observed. Solvent removed by boiling at 1 atm. Heat treatment: 300°C (under He atmosphere).

A. Dry (δ 0.35, Δ 1.10, Γ 0.73)*

B. In contact with 1 M NaOH (δ 0.35, Δ 0.70, Γ 0.49)*

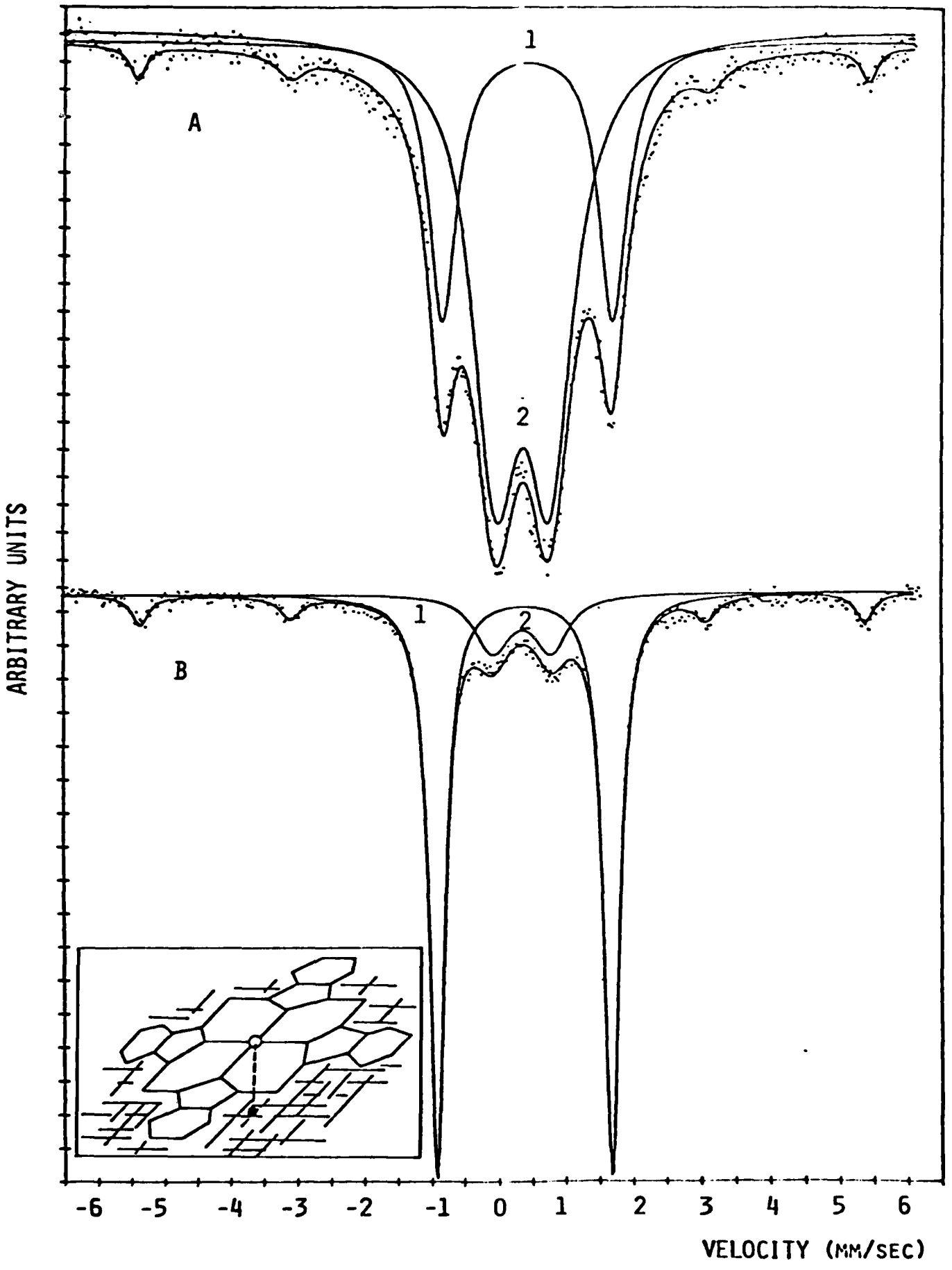
C. In contact with 0.5 M H_2SO_4 (δ 0.35, Δ 0.90, Γ 0.74)*

*Isomer shifts are given vs. α-Fe and all parameters in mm/s. Γ corresponds to line width at half peak height.

Figure 3. In situ electron conversion Mossbauer spectra for ^{57}Fe electroplated film on Au on Melinex in borate buffer (pH 8.4).

A. Cathodic protection region

B. Passive region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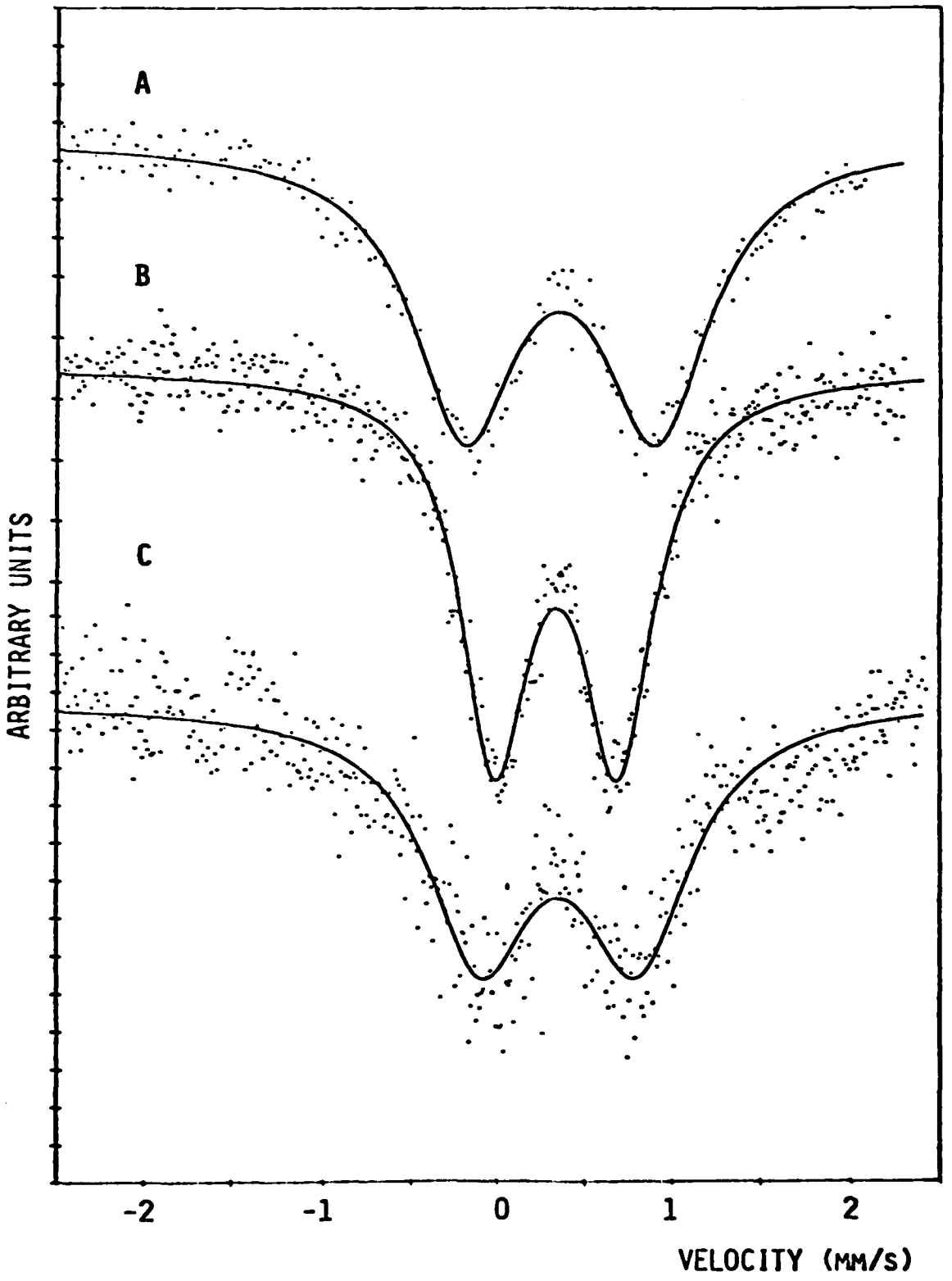
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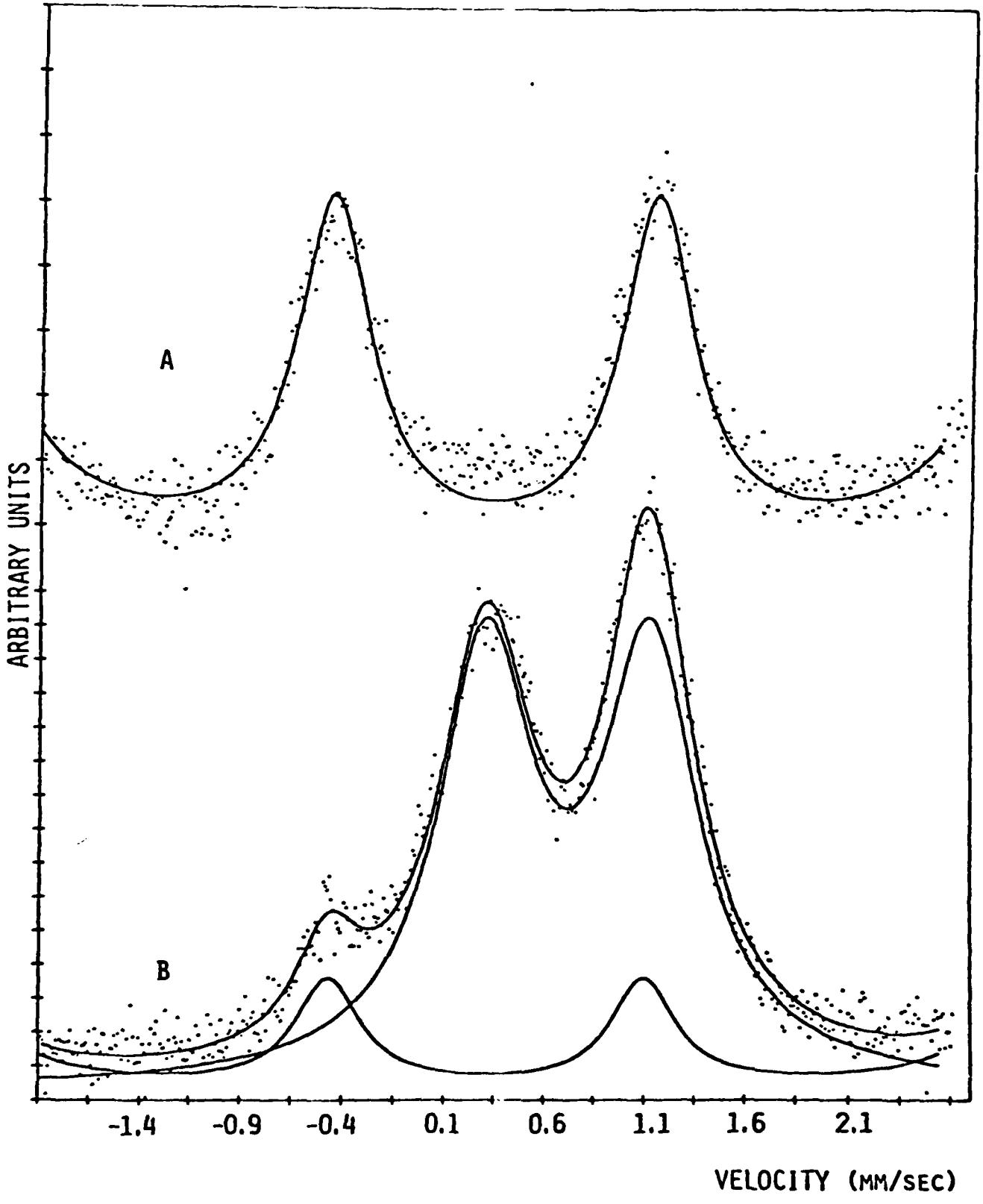
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