

Application of a Multiple Mössbauer Spectrometer to Electrochemical Processes in a Prussian Blue-Modified Carbon Electrode

T. L. Greaves and J. D. Cashion

School of Physics and Materials Engineering, Monash University, Victoria 3800, Australia.

A Mössbauer spectrometer capable of taking multiple spectra has been used to take a series of spectra in-situ of a Prussian Blue-modified carbon electrode. The eight spectra that were obtained clearly show that 10% of the high spin iron underwent a reversible redox reaction.

1. Introduction

A Multiple Spectrum Mössbauer data acquisition system has been recently developed which is capable of taking a series of time related spectra of a continuously cycling process [1,2]. Reversible electrochemical reactions involving a change in valency of iron are particularly suited for study by this spectrometer, where the electrochemical complex is part of a solid electrode.

We have applied this spectrometer to study a sample of insoluble Prussian Blue (IPB), $\text{Fe}_4^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, where the high spin ferric site was isotopically enriched with ^{57}Fe . While both iron sites are capable of undergoing reversible redox reactions, the ferric site was focussed on because, being high-spin, there is a greater difference in the Mössbauer parameters between the Fe^{2+} and Fe^{3+} forms, than for the low-spin ferrocyanide site.

In previous reports the spectra of IPB have been fitted with one singlet for the low-spin ferrocyanide site, and a very broad doublet for the high-spin ferric site. However, as Reguera et al. [3] have noted, the high-spin iron site should be fitted with a distribution of doublets because there are a number of possible combinations for the water and cyanide ligands around this iron site.

The Mössbauer spectrometer was used in-situ to record a series of 8 spectra of an IPB-modified graphite electrode operating as the working electrode in a cyclic voltammetry experiment. The spectra were used to observe the amount of high spin iron undergoing the redox reaction throughout the electrochemical process.

2. Experimental Method

The electrochemical cell was specifically designed to optimise in-situ Mössbauer spectra to be taken of the working electrode, and has been described previously [4].

A sample of crystalline IPB was prepared using the method of Buser et al. [5], where a diffusion method was used to slowly grow crystals over an 8 week period. The iron chloride precursor was prepared using isotopically enriched ^{57}Fe , so that only the high spin ferric site in the final IPB was isotopically enriched.

The working electrode was prepared by grinding 20mg of IPB with 180mg carbon powder. A small amount of Teflon was added as a binder, and the resulting paste spread onto the perspex electrode support in the cell and left to dry. The surface was smoothed with #1000 sandpaper, and rinsed with distilled water. A Ag/AgCl reference electrode and platinum mesh counter electrode were used with 1M KNO_3 as electrolyte. The voltage range -0.25 to 1.6V vs Ag/AgCl was scanned continuously and the trace recorded on an X-Y plotter.

Eight Mössbauer spectra were accumulated during the cyclic voltammetry. They were uniformly distributed around the loop with the first spectrum occurring at the most negative voltage.

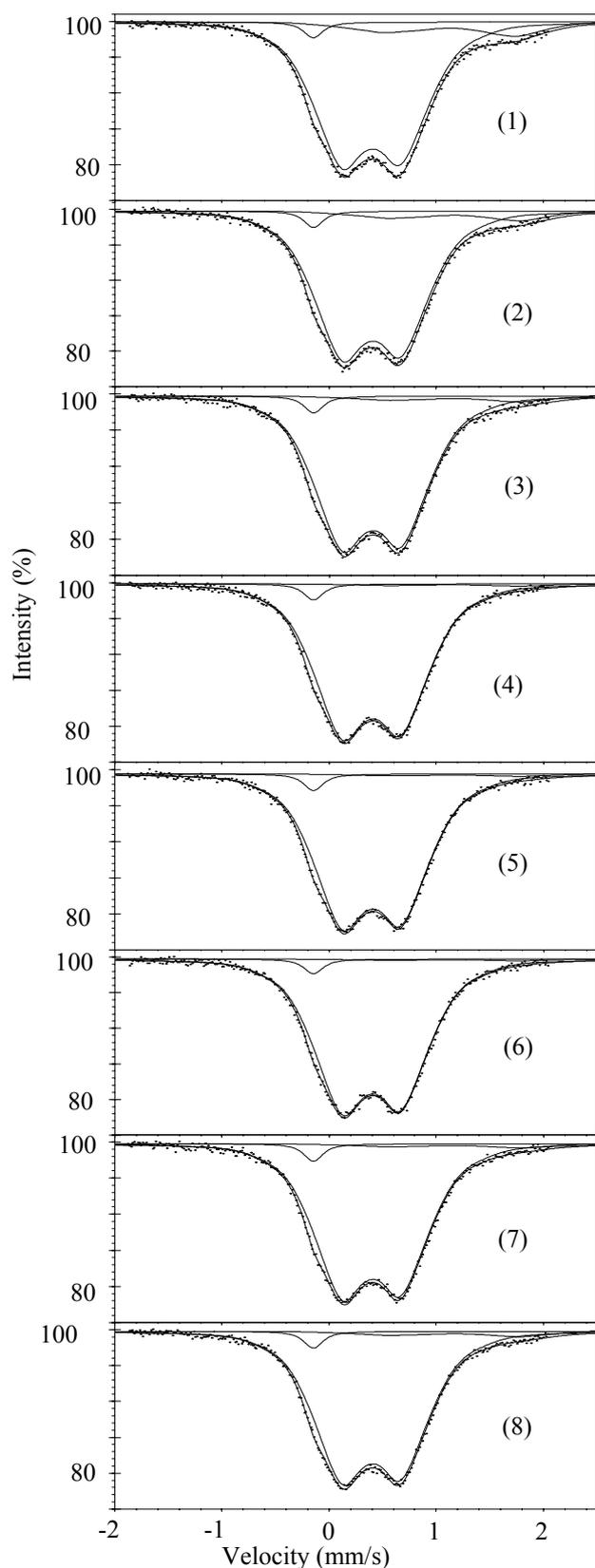


Fig. 2. Mössbauer spectra of the working electrode, where the spectrum number corresponds to the voltage range in Fig. 1.

3. Results

The cyclic voltammogram recorded is shown in Fig. 1. The peaks located at -0.10V and 0.35V vs Ag/AgCl are from the reduction and oxidation respectively of the high spin iron site [6]. The peak positions in the cyclic voltammogram were stable over the 2 days of data acquisition.

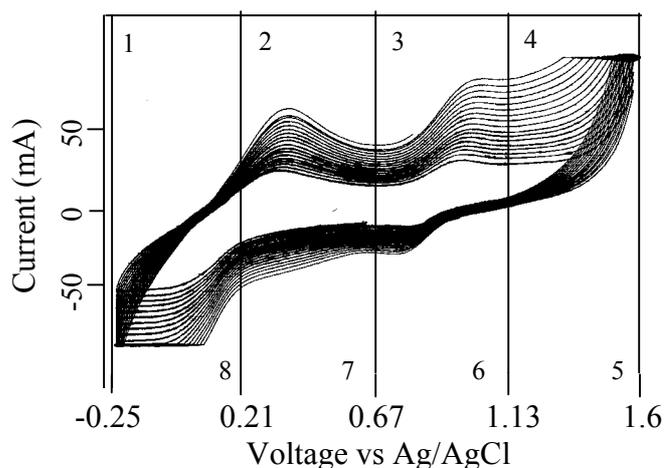


Fig. 1. Cyclic voltammogram of the IPB-modified graphite electrode, and voltage ranges over which the spectra were recorded.

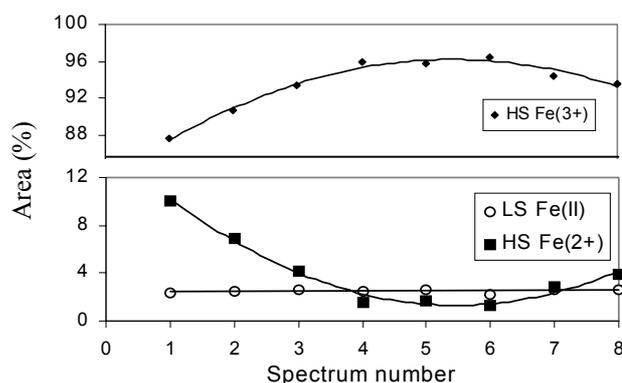


Fig. 3. Spectral areas for the three iron sites, where the spectrum number corresponds to the spectra shown in Fig. 2.

The series of 8 Mössbauer spectra are shown in Fig. 2, and were recorded over the voltage ranges as shown in Fig. 1, such that section 1 of the cyclic voltammogram corresponds to spectrum (1). The spectra were

all fitted with a singlet for the low spin ferrocyanide site, and distributions of doublets for both the ferric high spin site, and the electrochemically produced ferrous high spin site. The spectral areas are given in Fig. 3, and the fitting parameters for all 8 spectra in Table 1.

	IS (mm/s)	QS range (mm/s)	QS mean (mm/s)	
LS Fe ^{II}	-0.15	0		Table 1. Mössbauer parameters for all eight spectra.
HS Fe ³⁺	0.39	0 - 1.5	0.68	
HS Fe ²⁺ *	1.14	0.25 -2.25	1.16	

*There is a small negative correlation between the isomer shift and the quadrupole splitting.

4. Discussion

The spectra clearly show that 10% of the high spin iron took part in the electrochemical process. It is assumed that the rest was inaccessible to the potassium counter ions, and thus unable to participate. As expected, the largest amount of high spin ferrous iron was present in the voltage range which included the reduction peak. After the oxidation peak most of the high spin iron was returned to the ferric form, which showed the system was quasi-reversible.

Since the environment of the high spin iron atoms are a statistical distribution of cyanide and water ligands, this causes a range of quadrupole splittings. Consequently, each of the eight spectra were fitted using Voigtians, which represent a Gaussian distribution of Lorentzian lines. Table 1 lists the quadrupole splitting range used, and the mean value of the splitting, which was constrained to be the same for all the spectra. There is substantial disagreement in the literature for the Mössbauer parameters of Prussian Blue due to different preparation methods. The parameters for the low spin site and ferric high spin site agree fairly well with those given by Reguera et al. [3], while the parameters from Itaya et al. [7], agree well with the electrochemically produced high spin ferrous site, but not with the high spin ferric site.

The low spin iron site also underwent a redox process, contributing the peaks at 0.79V and 1.08V vs Ag/AgCl. However, the differences in the Mössbauer spectra between low spin ferro- and ferricyanide were negligible.

5. Conclusion

In-situ Mössbauer spectra of an Insoluble Prussian Blue-modified graphite electrode clearly show that 10% of the high spin iron underwent a quasi-reversible electrochemical redox reaction. The redox peaks for this iron site were centred on 0.13V vs Ag/AgCl.

Acknowledgments

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