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Multiple Mössbauer Spectra Data Acquisition with an In-situ Cyclic Voltammetry System

T L Greaves[1], J D Cashion[1], A L Benci[1], N K Jaggi[1,3] C Hogan[2] and A M Bond[2]
[1] *School of Physics and Materials Engineering, Monash University, Vic 3800, Australia*
[2] *School of Chemistry, Monash University, Vic 3800, Australia*
[3] *Physics Department, Illinois Wesleyan University, Bloomington IL 61702-2900, USA*
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A Mössbauer spectroscopy system has been developed which is capable of taking multiple Mössbauer spectra, which are related in time. Its present design is for operation in conjunction with an in-situ electrochemical cell, such that up to 256 Mössbauer spectra can be taken in a dedicated PC. These spectra are uniformly distributed around a cyclic voltammetry looP, which is continually retraced until sufficient statistics are accumulated. This system was used to acquire four spectra of a Prussian-blue-modified graphite paste electrode, while the electrode was involved in an electrochemical process. The spectra show differences due to the reduction and oxidation of the iron in Prussian blue.

Keywords: Cyclic voltammetry, Spectro-electrochemistry, Prussian blue.

1. Introduction

Conventionally, Mössbauer Spectroscopy involves the acquisition of a single spectrum completely before another is started. This imposes some limitations on the technique of Mössbauer Spectroscopy which are not inherent in the Mössbauer Effect, but only in its applications. Multiple Mössbauer Spectroscopy involves the acquisition of more than one spectrum during the same time period. This can be very beneficial in some circumstances, enabling the retention of information that would otherwise be lost, such as changes in the iron species across a sample, or throughout a time varying sample.

The previously developed Imaging Multiple Mössbauer Spectrometer (Smith et al., 1992), is capable of taking up to 256 spectra in a 1-dimensional array across a thin sample. The benefit of the imaging system is that it retains phase information of the iron compounds across the sample.

The present Time Dependent Multiple Mössbauer Spectrometer (TDMMS) was designed based upon the Imaging system to take multiple spectra over time throughout a cyclic process. From the series of spectra the iron species present at different stages of the cyclic process can be determined. Currently the system is designed to operate in conjunction with a specially designed in-situ electrochemical cell, in which a cyclic voltammetry process occurs while spectra are taken of the working electrode.

The Prussian-blue-modified graphite electrode was chosen for testing the equipment due to it being well characterised electrochemically (Dostal et al., 1995), and by Mössbauer spectroscopy (Reguera et al., 1992). The electrochemistry of soluble Prussian blue, $KFe^{III}[Fe^{II}(CN)_6]$, is complicated due to the two different iron sites present, which both can undergo oxidation and reduction. The reduction product is Everitt's salt, $K_2Fe^{II}[Fe^{II}(CN)_6]$, and the oxidation product Prussian yellow, $Fe^{III}Fe^{III}(CN)_6]$ (Dostal et al., 1995). In this investigation the TDMMS has been used to acquire four spectra of a Prussian-blue-modified graphite paste electrode while it is undergoing a cyclic voltammetry process.

2. Experimental

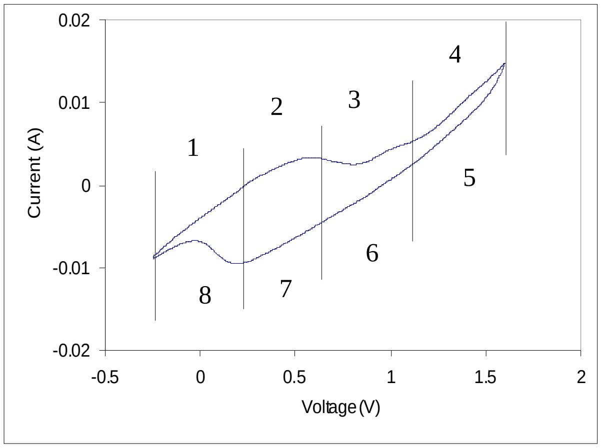
The TDMMS consists of a cyclic voltammeter coupled to a Mössbauer spectrometer, as shown in Figure 1. The cyclic voltammeter is driven by a triangular voltage applied to the in-situ electrochemical cell. This voltage is also converted into a sawtooth form, which ensures there is a unique relationship between this potential and any point in the cyclic voltammetry sweep. The arrival of a pulse corresponding to a 14.4 keV gamma triggers a sampling of the sawtooth potential by an analogue to digital converter. This digital signal is processed to determine into which spectrum number the count should be stored. The velocity information determines the channel number of the spectrum in the usual manner.

Currently the spectrometer is capable of taking up to 256 spectra at room temperature. It is designed flexibly so that the input can be changed to any other cyclic process, such as a magnetic hysteresis loop.The in-situ electrochemical cell used for these experiments was specifically designed to enable Mössbauer spectra to be taken of the working electrode while the electrochemical process is taking place. The design of the cell has been described elsewhere (Greaves et al.).

Insoluble Prussian blue powder was prepared according to the procedure in (Dostal et al., (1995) for Prussian blue I, and was electrochemically converted into soluble Prussian blue. Graphite powder was combined with the Prussian blue in a 5:1 ratio by weight, and 280mg of the mixed powders were stirred with approximately 200μL Teflon wax, then quickly transferred to the perspex support. Once dry, the surface was polished with fine sandpaper and rinsed with distilled water. A Ag/AgCl reference electrode and platinum mesh counter electrode were used with 4M KNO_3 as the electrolyte. The cyclic voltammeter swept through the voltage range between –0.25 to 1.60 V, at a scanning rate of 5mV/s.

3. Results

A cyclic voltammogram of the electrode is shown in Fig. 2. Traversing the trace clockwise from –0.25V we can see the features corresponding to the oxidation of the high spin iron site from Fe^{2+} to Fe^{3+} at 0.6V, and the reduction pair to this at 0.17V on the lower branch. The expected peaks for the oxidation and reduction of the ferrocyanide site were not seen, which was probably due to the positive potential not going sufficiently far. The data acquisition too place over 6 days, and the stability of the cyclic voltammetry trace was monitored on a chart recorder, with the voltages of the peaks remaining constant.



Eight Mössbauer spectra were acquired at room temperature using a constant acceleration drive. These spectra were then combined to give four non-equivalent spectra in the potential ranges (a) –0.25 to 0.21V, (b) 0.21 to 0.68V, (c) 0.68 to1.14V, (d) 1.14 to 1.6V. These spectra are shown in Fig. 3, and the mean fitting parameters in Fig. 4.

Fig. 2: Cyclic voltammogram of the working electrode between –0.25 to 1.6V.

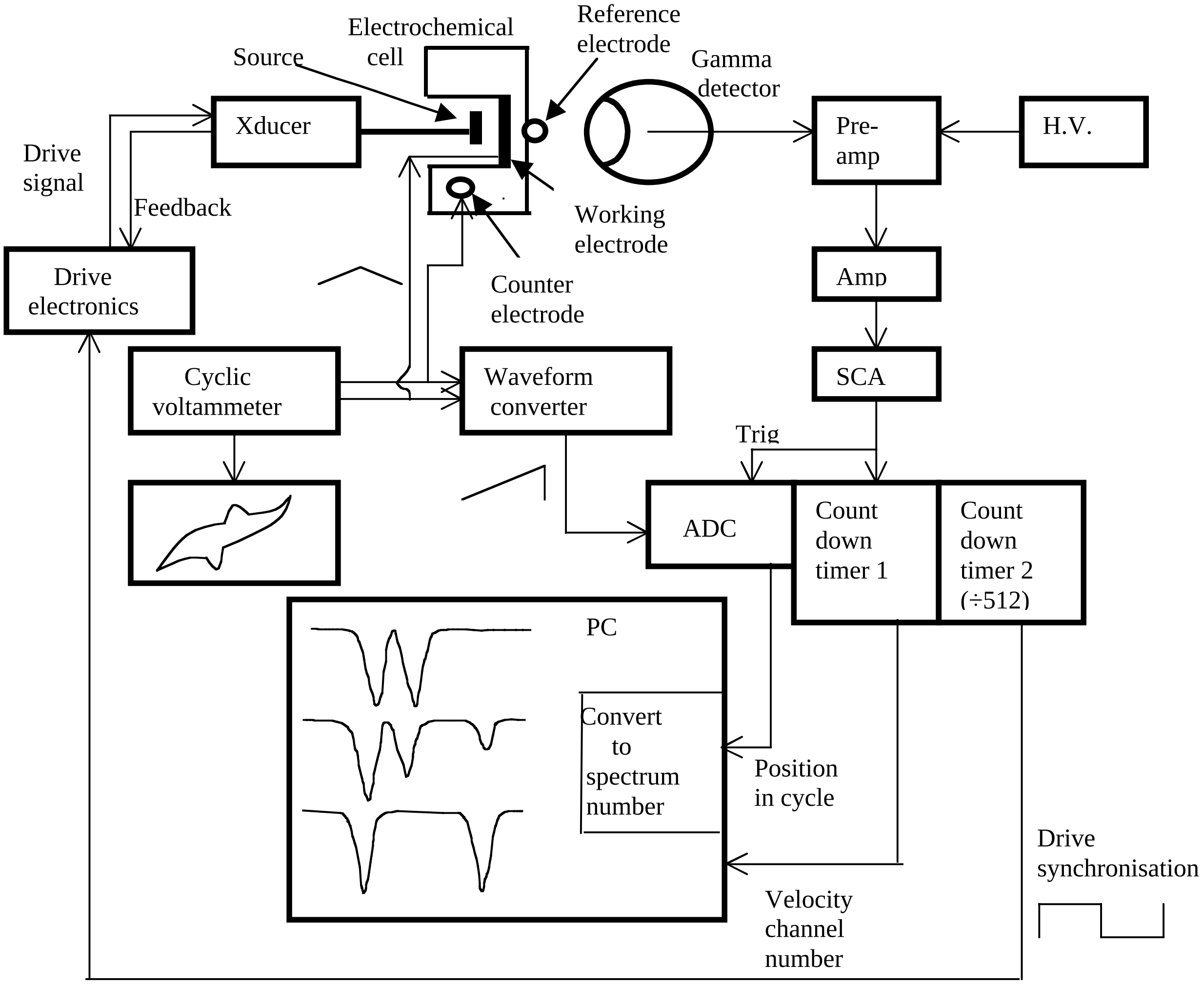


Fig. 1: Schematic diagram of the equipment.

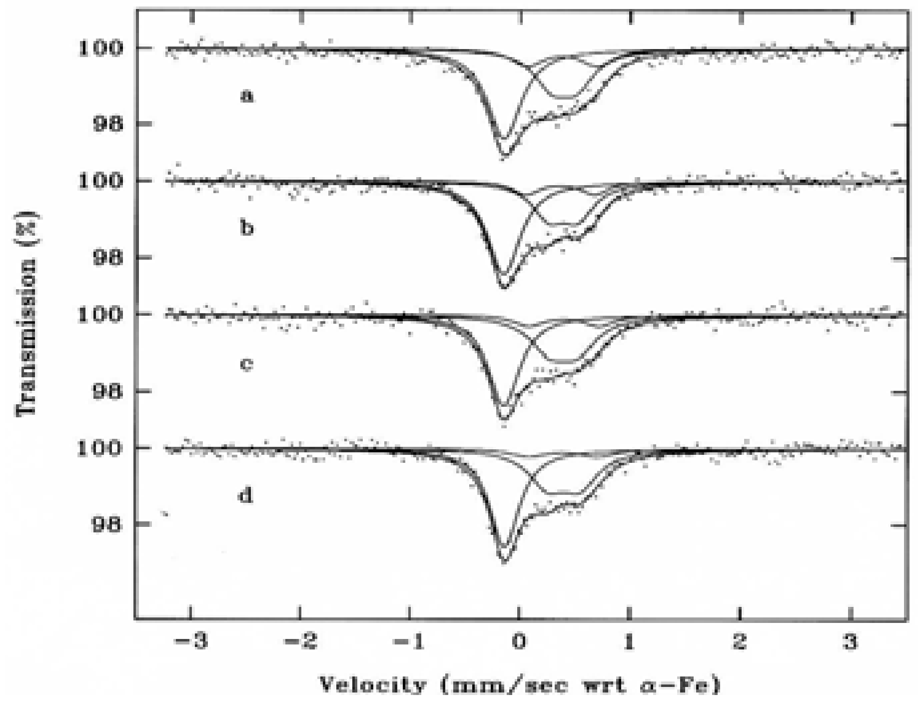
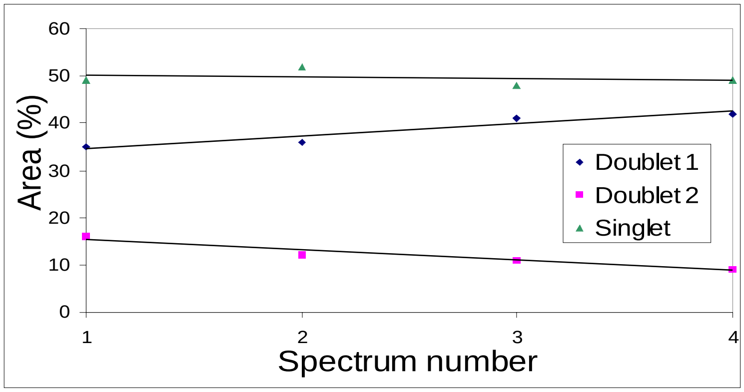


Fig. 3: Mössbauer spectra of the cyclic system, for the four different potential ranges.



	IS (mm/s)	QS (mm/s)	Γ (mm/s)
Doublet 1	0.39	0.27	0.40
Doublet 2	0.38	0.64	0.35
Singlet	-0.15		0.35

Figure 4: Mean fitting parameters for the spectra. The singlet and doublet 1 correspond to the standard parameters for soluble Prussian Blue.

4. Discussion

The four Mössbauer spectra obtained showed a general trend which was consistent with the partial reduction and re-oxidation of soluble Prussian blue during the cyclic process. The parameters for the low spin Fe^{II} site and the high spin Fe^{III} site present in all four spectra agree well with the parameters for soluble Prussian blue as given in (Reguera et al., 1992). The doublet with the larger quadrupole splitting decreased with increasing applied potential. This doublet corresponds to the reduced high spin iron site. The results are consistent with the cyclic voltammetry data. No changes were detectable in the spectra for the oxidation of the low spin ferrocyanide site.

No previous Mössbauer spectra have been taken of the electrochemically produced oxidation and reduction products of Prussian blue. This is probably due to their instability with no applied potential. The instability of the products is not an issue with the TDMMS, since the process is continually cycling. This new system extends the types of possible spectra which can be taken using Mössbauer spectroscopy.

5. Conclusion

Multiple Mössbauer spectra were obtained throughout a periodic cycling of an electrochemical system consisting of a Prussian-blue-modified graphite paste electrode. The Mössbauer spectra taken of the Prussian blue showed partial reduction of the high spin iron site at 0.5V, but no change due to the oxidation on the low spin iron site.

Acknowledgements

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