Conversion of the Broad EPR Signals to Intermediate Linewidth During the Electrochemical Reduction of Carbon Blacks in Dispersion

by

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Abstract The electrochemical reduction of carbon black particles dispersed in methylene chloride was monitored in situ with EPR spectroscopy. The broad EPR signal due mainly to charge carriers is converted to a signal with intermediate linewidth (ΔH_{pp} ~22G) in both CSX-99 and BP-1300 carbon blacks. This narrowing was coincident with the manifestation of the narrow EPR signal (ΔH_{pp} ~5G) due to reduction of localized surface states. Possible causes for these EPR changes upon electroreduction are discussed.

Introduction

The charging of toner particles in the xerographic process is dependent on the type of carbon black which is incorporated into the toner[1]. In an effort to study the nature of charge exchange with carbon blacks, we have developed a simple electrochemical cell which allows for "in situ" EPR detection[2,3]. It was previously demonstrated that narrow (ΔH_{pp} ~ 5G) EPR signals were generated upon electroreduction of carbon blacks in dispersion[2]. Further efforts revealed that these narrow signals were the result of unpaired electrons at localized sites[3]. Since the magnitude of these narrow signals correlated roughly with degree of surface oxidation (or adsorbed benzoquinone), it was suggested that the origin of these signals was reduced, localized surface states.

In the present report we have extended these electrochemical studies of carbon blacks with a focus on the broad EPR signals (ΔH_{pp} between 50 and 100G). The broad signals are mainly reflective of charge carriers and as such exhibit Pauli paramagnetism[4,5] (Intensity is independent of temperature).

Experimental

In these initial experiments we have used a relatively simple two electrode electrochemical cell. The major objective of this type of cell design was to ensure that the carbon black particles make good electrical contact with the electrode.

The EPR spectrometer system was a Varian E109 system interfaced with a Nicolet 1180 computer. Simulations of EPR spectra were carried out with programs provided by Nicolet. Variable temperature was achieved with a Varian Model E-257 Variable temperature controller.

BP1300 and CSX-99 were obtained from Cabot Corporation. CSX-99 is the unoxidized precursor to BP1300. Their properties have been previously summarized.[3]

Results and Discussion

The EPR spectrum of CSX-99 in nitrogen purged methylene chloride is shown in figure 1. The four narrow lines are due to 4 of the 6 Mn^{+2} lines present in the reference sample of SrO. The linewidth, ΔH_{pp}, is 66G and the apparent g-factor is 1.999. (There is some Dysoniandistortion of the lineshape due to microwave skin effects and consequently the g-factor is underestimated by using the cross-over point). The

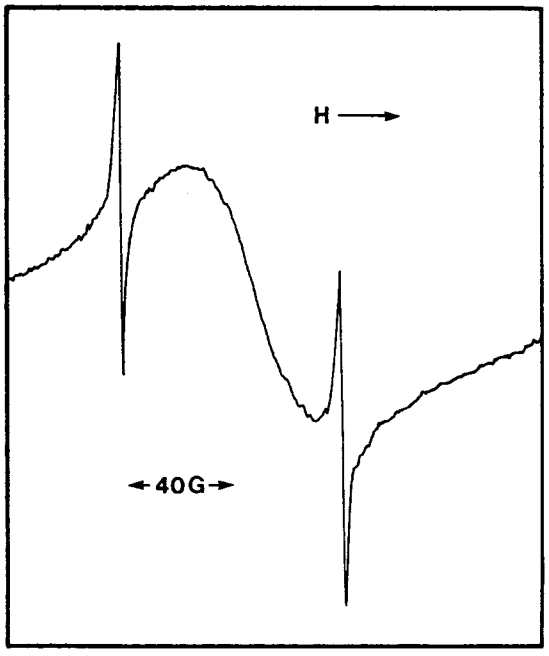

Figure 1. EPR Spectrum of CSX-99

temperature dependence of this signal (the intensity or second integral of the spectrum) reveals that ~75% of the signal is due to charge carriers (i.e. it is temperature independent and therefore Pauli paramagnetic).

Electro-oxidation brings about no change in the spectrum whereas electroreduction causes significant changes in the observed spectrum (see figure 2). This spectrum can be simulated using Lorentzian lineshapes with a broad, 66G signal with g = 1.999, a narrow, 5G signal with g = 2.0027 and

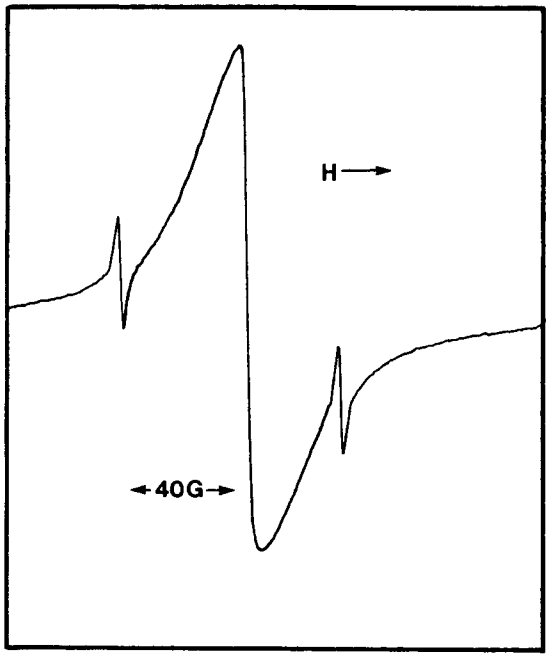

Figure 2. EPR Spectrum of CSX-99 - After electroreduction

an intermediate signal with ΔH_{pp} of 22G and g = 2.0020. In this case the percentage of spins associated with each signal is : broad - 47%; intermediate 51% and narrow 2%. The change in intensity before and after electroreduction was less than 5%. These results suggest that electroreduction is changing the environment of some of the spins in the carbon black. Since oxygen is known to have profound effect on the linewidth of most carbon blacks,[4] it is postulated that under these conditions O_2 which is occluded or strongly adsorbed is electrochemically reduced to H_2O_2 (or HO_2^-). This in turn would cause a decrease in ΔH_{pp} of the broad signal. The narrow signal arises from the population of localized surface states as previously demonstrated.[3]

The intermediate signal with ΔH_{pp} = 22G would then reflect the intrinsic linewidth of the carbon black particles. The temperature dependence of the intermediate signal reveals that ΔH_{pp} narrows as the temperature is lowered. This can be contrasted to the broad signal (figure 1) which broadens slightly at lower temperatures.

Hence electroreduction of CSX-99 carbon black particles converts the broad signal into an intermediate signal with ΔH_{pp} = 22G. Similar results were obtained with the oxidized CSX-99 (BP-1300). It seems likely that the mechanism involves reduction of molecular O_2.

References

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