

The Redox Characteristics of Biochar and Hydrochar

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Introduction

Biochar is proving itself to be a valuable additive to soils to improve fertility and ultimately crop yields for human consumption or energy production. Considerable effort has been expended in trying to understand the mechanism through which biochar improves soil fertility, although at this time conclusive evidence is not available.

One possible mode of action is through the electrochemical characteristics of the biochar relative to the soil. Certainly the soil and groundwater composition contribute to the chemistry of the environment. However, the potential (Eh) and acidity (pH) of the terrestrial environment will also contribute to the nature of the species present; i.e., oxidation state, and hence their bio-availability. An important point to note is that these Eh and pH conditions (and hence speciation) are changeable and in most cases react to changes in the local environment.

Biochar, like many carbon-based materials (e.g., coal, activated carbon, carbon black, etc.), can exhibit redox and charge storage capabilities depending on its intrinsic physico-chemical properties. Redox activity (Faradaic processes) originates from charge transfer associated with functional groups on the carbon surface or from ionic intercalation into the char structure. Alternatively, charge can be stored at the char-electrolyte interface within the double layer (non-Faradaic processes).

Results and Discussions

In this paper we report on our efforts to characterize the electrochemical behaviour of a number of char samples prepared either conventionally by pyrolysis of an organic matter precursor, or hydrothermally from a waste wood precursor.

Electrochemical characterization was achieved initially by cyclic voltammetry (CV) on a composite electrode of char and graphite (1:10 by weight) in a buffered pH 7 electrolyte, an example of which is shown in Figure 1.

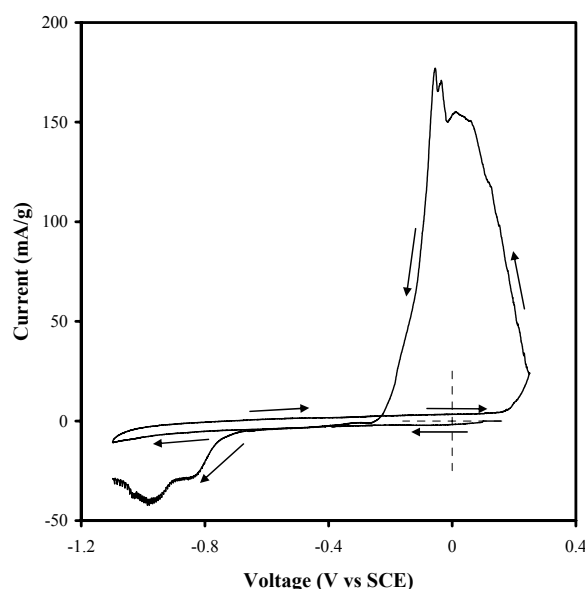


Figure 1. Typical CV of biochar (0.05 mV/s).

Starting at ~0.15 V the first cathodic scan liberates very little cathodic charge. That which is measured is associated with non-Faradaic discharge of the double layer at the char-electrolyte interface. Upon sweep reversal similar non-Faradaic phenomena occur until the upper voltage limit is reached. However, upon sweep reversal again it is clear that the char undergoes an activated oxidation process that liberates considerable charge. What is surprising is that it happens at lower voltages implying the higher voltage anodic treatment has changed the char-electrolyte interface to make more charge available. This may be associated with either chemical changes to the char surface, or more likely physical changes to the interface through pore opening, for example. At even lower voltages after the second cathodic scan the surface is more redox active with a greater cathodic current flowing. Most biochar and hydrochar samples we have examined exhibited similar behaviour, the difference being the magnitude of the activated anodic current.

We have also conducted a series of electrochemical impedance spectroscopy (EIS) experiments, coupled with step potential electrochemical spectroscopy (SPECS) on similar char electrodes to characterize the charge storage mechanisms. The electrochemical protocol applied is shown schematically in Figure 2, with EIS spectra collected at the end of each step, while selected data is shown in Figures 3(a) and (b).

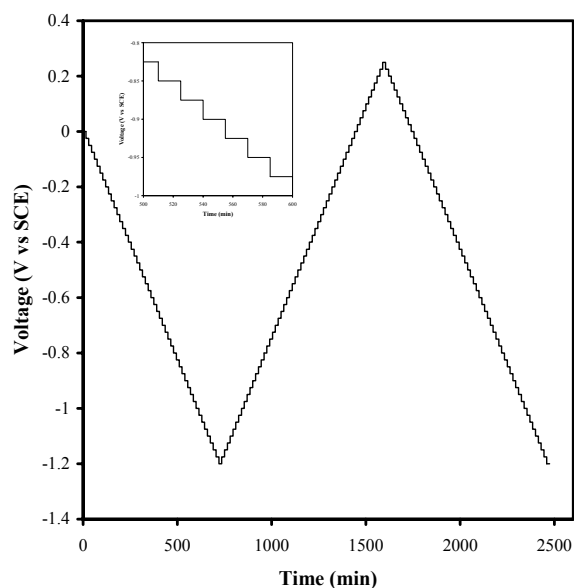


Figure 2. Electrochemical protocol for the EIS experiments.

In this case there was considerable variation in the EIS data depending on the applied voltage. It shows a range of different phenomena occurring, including the effects of electronic conduction, charge storage in the double layer, and mass transport of species within pores, all as a function of state of charge.

Coupled with this we have also conducted a range of SEM, XPS and gas adsorption measurements on the char samples both before and after electrochemical cycling. Based on these experiments, the electrochemical activity of the chars will be discussed.

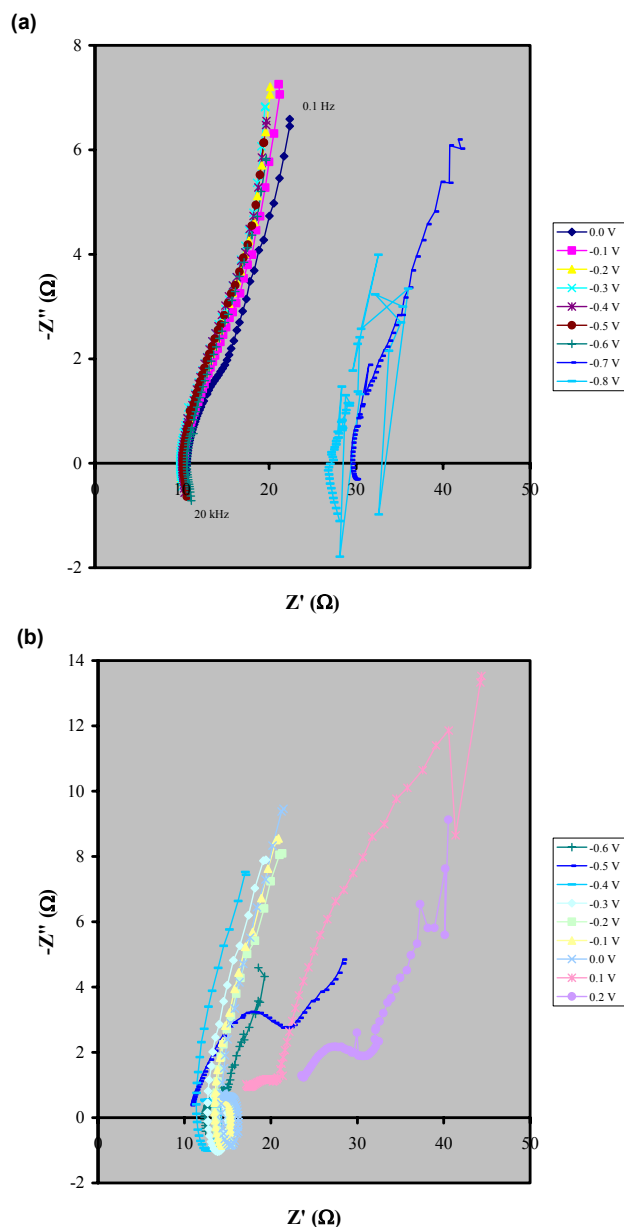


Figure 3. EIS data during (a) the first cathodic and (b) anodic sweep.

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