

## The Reversibility of Super-Iron Cathode Materials using In situ Mossbauer and Synchrotron x-ray spectroscopy

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### Introduction

This investigation examines the nature of Fe (VI) chemistry during charge and discharge process in aqueous KOH electrolyte. This is motivated by the need for high capacity cathode materials for both aqueous and non-aqueous battery communities. We will present in situ spectro-electrochemical data on the discharge and charge characteristics of  $K_2FeO_4$  using Mossbauer and synchrotron x-ray (XRD and XAS) spectroscopy. Details of the structural transitions (both from the point of view of long and short range atomic order) and electronic state changes in the iron will be presented. Our data such as those obtained from in-situ Mossbauer spectroscopy clearly shows that  $K_2FeO_4$  is a reversible cathode. Future prospects of this material for application in non-aqueous batteries will be discussed.

### Experimental

$K_2FeO_4$  of 99% purity was synthesized using methodology described elsewhere<sup>1,2</sup>. The in-situ cell was fabricated with  $K_2FeO_4$  and graphite composite cathode, zinc anode with 13.5 M KOH electrolyte. The in-situ Mossbauer was measured with a spectrometer working in constant acceleration mode using 1024 channels for data storage and with the  $^{57}Co^{Rh}$ -radiation source. High resolution in situ XRD and XAS spectra was measured at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL), Upton, NY using beam lines X-7A and X-11A respectively. Details of the beam line optics and data analyses are given elsewhere<sup>3</sup>.

### Results and Discussion

Figure 1 (a) represents the Mossbauer spectrum at the beginning of discharge with the cell potential at 1.65 V. A single resonance line was observed at isomer shift of  $-0.72$  mm/sec at 298 °K. This clearly points to Fe (VI) oxide ( $K_2FeO_4$ ) in agreement with earlier reports<sup>4</sup>. Figure 1 (b) shows the in-situ Mossbauer spectrum after 20 hrs discharge with cell voltage at 0.8 V. This corresponds to the appearance of a doublet with isomer shift of 0.4795 mm/sec, corresponding to a

Fe (III) compound<sup>4</sup>. A concomitant decrease in  $Fe^{6+}$  ion concentration is also evident. The presence of a singlet at the end of discharge indicates the presence of Fe (VI) species at the end of discharge. Analysis of the spectrum shows that the amount of Fe (VI) species at the end of discharge corresponds well with the difference between the observed capacity and the theoretical maximum. During the charge process, shown in figure 1c & d the spectrum shows the decrease in  $Fe^{3+}$  concentration, indicated by the decrease in doublet intensity. The concomitant increase in  $Fe^{6+}$  concentration is indicated by increase in the singlet intensity during charge process. This clearly indicates that the conversion of  $Fe^{3+}$  to  $Fe^{6+}$  was incomplete, as the doublet for  $Fe^{3+}$  does not disappear completely. The poor conversion efficiency might be because of lack of understanding of the real Fe (III) oxide structures that are responsible for this reversible behavior. In addition, there is interplay of many other factors such as depth of discharge, hydroxide concentration etc.

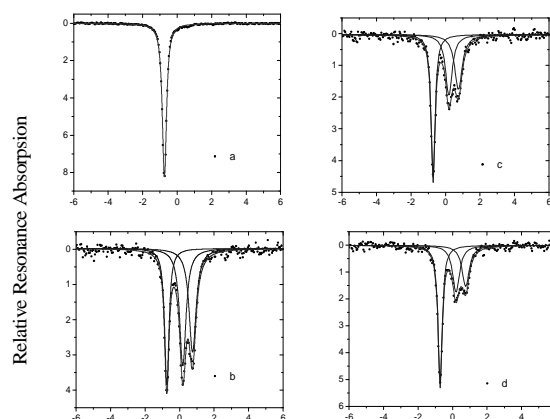


Figure 1. Velocity relative to Fe foil (mm/s)

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