Aqueous Fe (VI) Batteries: Correlation of Electrochemistry with *In situ* Mössbauer and Synchrotron X-ray Spectroscopic Investigation

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Super iron batteries use high oxidation state Fe(VI) compounds as cathode materials and show large specific capacity compared to the commercial MnO_2 batteries[1]. The large specific capacity is due to the three electron transfer in the discharge process[2]. It is also reported that super iron batteries can be recharged multiple times in aqueous media using a Na_2FeO_4 nanofilm synthesized electrochemically[3] as cathode material. The thicker electrodes are more easily polarized compared to the nano-thick electrodes.

K_2FeO_4 which shows partial reversible behavior in aqueous media *vs.* Zn anode forms an amorphous Fe (III) compound.[2] However, the identity of the discharge product still remains unknown. In this presentation, the authors will show results on the discharge behavior of a variety of Fe (VI) compounds. The nature of change in terms of lattice parameters, phase morphology and oxidation states will be presented with data from low temperature Mössbauer spectroscopy and synchrotron based *in situ* X-ray absorption and diffraction spectroscopy.

Experimental:

K_2FeO_4 is synthesized by oxidation of $Fe(NO_3)_3$ using hypochlorite ions prepared by purging Cl_2 gas into KOH solution as described elsewhere[2]. $BaFeO_4$ is synthesized from K_2FeO_4 analogs. Details of the method are given elsewhere[4].

Mössbauer experiment was conducted using a 25mCi, ^{57}Co in Rh lattice source. High resolution *in situ* XRD and XAS spectra are measured at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL), Upton, NY using beam lines X-7A and X-11A respectively with *in situ* electrochemical cells. Details of the beam line optics and data analysis are given in details elsewhere[5]. SEM images are obtained with a SEM/EDAX set up (Hitachi S4800).

Results and discussion:

The analysis of the EXAFS data at the Fe K edge under in situ conditions indicate that the fully discharged material resembles that of the hematite. This is in agreement with shifts in the Fe K edge XANES spectra measured as a function of electrode discharge.

Fig.1 shows the discharge behavior of $BaFeO_4$ and K_2FeO_4 in alkaline media *vs.* a Zn anode where a large plateau at 1.6 V and a small plateau around 1.3 V are both seen. The discharge behaviors of $BaFeO_4$ with several different carbon additives are also shown. It can be seen clearly that there are mainly two kinds of discharge curves

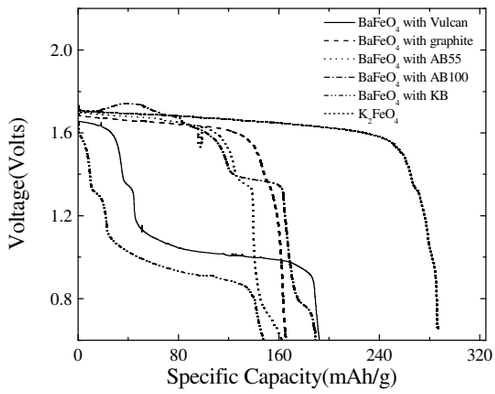

Fig. 1 Discharge behavior of $BaFeO_4$ and K_2FeO_4 *vs.* Zn anode

in these five carbon additives. One has large discharge capacity at 1.6 V and the other shows large discharge capacity at relatively smaller voltage region around 1 V as seen for Vulcan carbon and Ketjen black. A small plateau around 1.3 V is observed for all these additives and the largest capacity at 1.3 V is achieved with AB100 additive.

Acknowledgements:

The authors gratefully acknowledge start up grants from Northeastern University and support from Department of Energy, Materials Science Division for financial assistance in building and maintaining the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY).

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