

## Negative Electrodes Based on the $\text{Fe}_x\text{Zn}_{1-x}$ Alloy System

L.A. MacEachern<sup>a</sup>, R.A. Dunlap<sup>a,b</sup> and M.N. Obrovac<sup>a,b,c</sup>  
 a - Dept. of Physics and Atmospheric Science, Dalhousie University, Halifax, N.S. B3H 4R2 Canada  
 b - Institute for Research in Materials, Dalhousie University, Halifax, N.S. B3H 4R2 Canada  
 c - Dept. of Chemistry, Dalhousie University, Halifax, N.S. B3H 4R2 Canada

### Introduction

Alloy negative electrode materials are of interest for use in Li-ion rechargeable batteries due to their high volumetric capacity. Zn and Al have similar alloying properties with Li. Each react with one equivalent of Li, corresponding to volumetric capacities of 1478 Ah/L, and 1411 Ah/L, respectively. This is more than double the volumetric capacity of graphite. The cycle life of crystalline Zn and Al is poor because of 2-phase regions encountered during their lithiation.

In an attempt to improve cycle life, Al-M (M = a transition metal) alloys have been studied [1-3]. These studies showed that amorphous Al-based alloys can be formed when the M content is increased; however the capacity in these amorphous alloys is near zero [1-3].

Despite their similarities, Al-based alloys have been studied extensively as negative electrodes, while Zn containing alloy materials have not been well explored. In the present work the structure and electrochemistry of  $\text{Fe}_x\text{Zn}_{1-x}$  compounds is examined to determine if amorphous Zn-M alloys can be made that are active in lithium cells.

### Experimental

Thin film libraries of  $\text{Fe}_x\text{Zn}_{1-x}$  ( $0 < x < 0.55$ ) were prepared by DC magnetron sputtering. The film compositions were characterized by electron microprobe and X-ray diffraction (XRD). Electrodes were cycled in 2325 coin type cells between .005 V and 1 V at a rate of C/40 and trickled to C/80 with Li metal counter electrodes and 1M LiPF<sub>6</sub> in EC/DEC (1:2 v/v) with 10% FEC by volume electrolyte at 30°C. Thin films were also sputtered on Kapton substrate and analyzed with <sup>57</sup>Fe Mössbauer spectroscopy.

### Results and Discussion

Figure 1 shows the XRD patterns of sputtered  $\text{Fe}_x\text{Zn}_{1-x}$  films. As the Fe content increases, the film becomes amorphous and is completely amorphous when  $x > 0.18$ . To our knowledge, this is the first report of amorphous  $\text{Fe}_x\text{Zn}_{1-x}$ . Mössbauer spectra of the library are consistent with those reported for crystalline alloys of similar composition [4] and indicate there are three distinct Fe atomic environments in the material.

Figure 2 shows the cycle 5 charge capacity as a function of Zn content in the alloy. All alloys comprising crystalline Zn ( $x < 0.1$ ) showed activity with lithium. All such alloys had poor capacity retention, likely due to the crystallinity of the active phase. When  $x > 0.1$ , the capacity dropped to zero. This composition is coincident with alloys having a substantial amorphous content. This suggests that as an amorphous phase is introduced

essentially all of the Zn is being rendered inactive due to the distribution of Fe neighbors. These findings are similar to those found for the  $\text{Al}_x\text{Fe}_{1-x}$  system [2]. The electrochemistry and atomic environments of Fe in the thin film materials will be discussed.

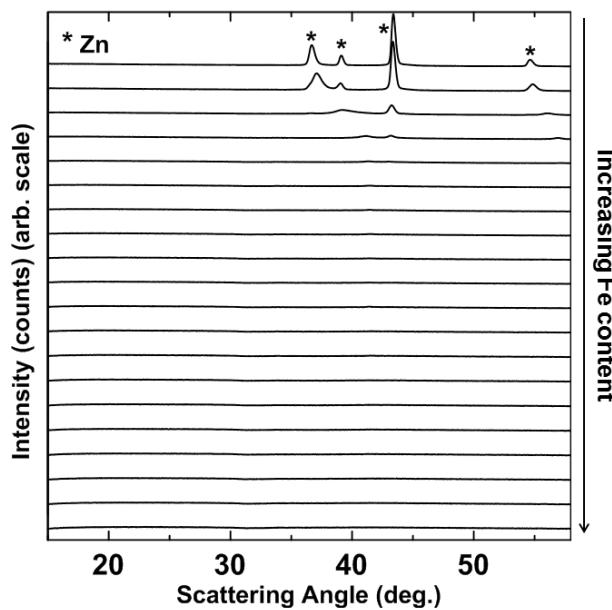


Figure 1 XRD spectra for  $\text{Fe}_x\text{Zn}_{1-x}$  for  $0 < x < 0.35$ .

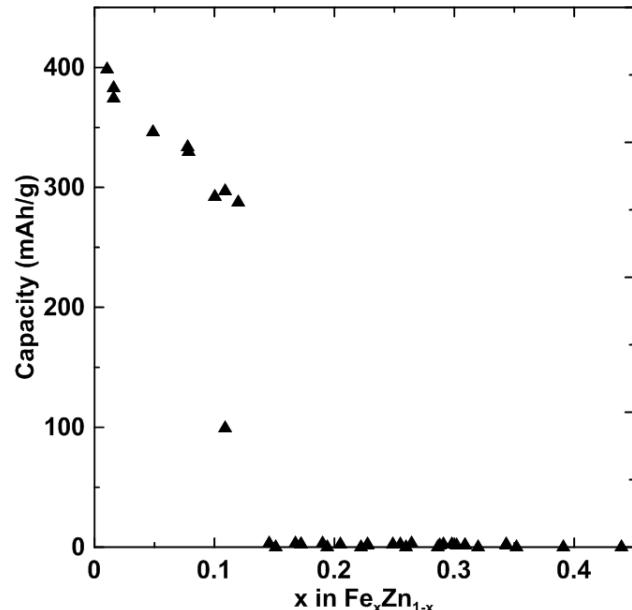


Figure 2 Fifth cycle discharge capacities for  $\text{Fe}_x\text{Zn}_{1-x}$  for  $0 < x < 0.55$ .

### References

- [1] M.D. Fleischauer, J.M. Topple and J.R. Dahn, *Electrochem. Solid-State Lett.* **8** (2005) A137-A140.
- [2] A.D.W. Todd, P.P. Fergusun, M.D. Fleischauer and J.R. Dahn, *Int. J. Energy Res.* **34** (2010) 535-555.
- [3] M.D. Fleischauer *et al.* *J. Electrochem. Soc.* **153** (2006) A484-A491.
- [4] A. Hauet, A. Laggoun and J. Telliet, *J. Mater. Sci. Eng.* **148** (1991) 123-129.