

Investigation of $\text{Na}_x\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ ($1.0 \geq x \geq 0.75$) for Na-Ion Battery Positive Electrodes

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Introduction

Fe-containing Na-ion cathode materials are attractive due to their relatively low cost, low toxicity and use of highly abundant raw materials. $\alpha\text{-NaFeO}_2$ has been shown to have poor electrochemical properties in Na-ion half cells with high voltage hysteresis, low capacity retention and only 80 mAh/g reversible capacity when cycled between 2.5-3.4V [1]. Large hysteresis at higher voltage windows may be a result of Fe migration into the Na layer [1]. Substitution of Mn [2] for Fe in layered phases improves electrochemical performance, resulting in a reversible capacity of 190 mAh/g for P2- $\text{Na}_{2/3}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$, however the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox couple remains associated with capacity fade for these materials [3]. Here, we investigate the $\text{Na}_x\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ system, having a solubility limit near $x = 0.72$ [4] to help further the understanding of iron containing sodium transition metal oxide cathodes.

Experimental

Fe_3O_4 , TiO_2 and Na_2CO_3 were mixed in stoichiometric amounts, ball milled and heated in air using temperatures described by Li et. al. [4]. to obtain samples of $\text{Na}_x\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$. Electrodes were prepared in a slurry mixture with 80% by weight $\text{Na}_x\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$, 12% Super-S carbon black and 8% PVDF binder dissolved in NMP. The slurries were spread on Al foil with a doctor blade and dried at 120 °C for several hours. 1.267 cm² circular electrodes were prepared from the coatings and incorporated into 2325 size coin-type cells using 1M NaPF₆ dissolved in PC. Two Celgard separators, one polypropylene blown microfiber separator (3M Company) and a sodium foil counter/reference electrode were used and assembly took place in an Ar filled glovebox. X-ray diffraction (XRD) measurements were performed using a Siemens D500 diffractometer using a Cu K_α source.

Results

The top panel of Figure 1 shows the XRD pattern of $\text{Na}_{0.8}\text{Fe}_{0.8}\text{Ti}_{0.2}\text{O}_2$, which is phase pure and has the O3 structure. The XRD pattern of this material after charging to 4.4V (removal of 0.3 Na) is shown in the middle panel and in Figure 2. The peaks between 50-70° are split in the XRD pattern of the charged material, indicating monoclinic distortion of the O3 unit cell. Unlike $\alpha\text{-NaFeO}_2$, no Fe diffusion into the Na layer could be detected.

Upon discharging $\text{Na}_{0.5}\text{Fe}_{0.8}\text{Ti}_{0.2}\text{O}_2$ to 1.5 V, a composition of $\text{Na}_{0.86}\text{Fe}_{0.8}\text{Ti}_{0.2}\text{O}_2$ is obtained, which has an identical O3 structure as the starting material, as shown in the bottom panel of Figure 1. The hysteresis observed in the voltage curve of these materials may be caused in part by energy loss during the monoclinic distortion that occurs during desodiation.

The consequences of structural changes during the

cycling of iron containing sodium transition metal oxide cathode materials and similarities between the $\text{Fe}_x\text{Ti}_{1-x}$ and $\text{Fe}_x\text{Mn}_{1-x}$ systems will be discussed.

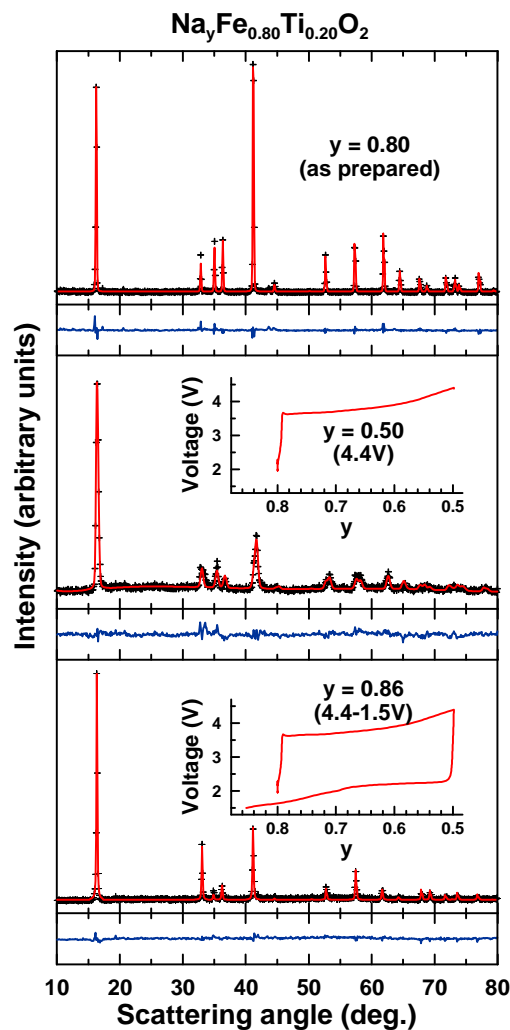


Figure 1

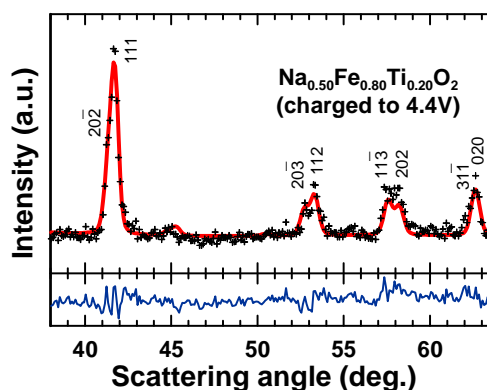


Figure 2

References

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