Electrochemical properties and thermal characteristics of FeOF cathode for Na-ion batteries

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Introduction

Recently ambient temperature sodium-ion batteries have drawn interest as a power source for large-scale grid energy storage due to the low cost and abundant resources of sodium. Up to now, lots of cathode active materials have been proposed for Na-ion battery. However, the lower gravimetirc and volumetric energy density of Na than Li is a major issue to be solved. Moreover, thermal stability is also one of concern, due to the high reactivity of Na against air. In order to improve the cost performance of Na-ion batteries, iron based conversion type cathodes are attractive such as Fe_2O_3, FeF_3, FeS_2. Among them, Iron oxyfluoride (FeOF) had been also proposed as a cathode material for Li-ion batteries and obtained a large practical capacity due to conversion reactions [1, 2]. In this study, FeOF was applied as the cathode material for Na-ion batteries. The electrochemical properties was studied and the charge/discharge mechanism during cycling were investigated by XRD, XPS, and Fe-K-edge XANES. On the other hand, by using TG-DSC and TG/DTA-MS system, the thermal characteristics of FeOF cathode in Na-ion batteries were also discussed.

Experimental

FeOF was synthesized by a reaction of 1:2.33 molar ratio of nanosized Fe_2O_3 (Sigma-Aldrich) and FeF_3 (Soekawa Chemicals Co.) at a temperature over 1000^{o}C in a roll-quench machine (Harddays Co. Ltd). The obtained FeOF flake was ground with acetylene black using a planetary ball milling machine at a weight ratio of 75:25. Then the composites were mixed with polyacrylate (Ethanol dissolved) at a weight ratio of 95:5 and dissolved in 1-methyl-2-pyrrolidinone. The slurry was coated on an Al foil and dried. The electrochemical measurements were carried out with a 2032 coin-type two-electrode cell, with Na foil as a counter electrode and 1 mol cm^{-3} $NaClO_4$/PC (Tomiyama Pure Chemicals Co.) as a electrolyte. The cells were cycled at constant current densities of 10 mA g^{-1} (0.02 mA cm^{-2}). For thermal analysis, the cycled electrodes were taken out from the disassembled cells, rinsed and soaked in DMC solvent, and then vacuum dried. Finally the active material powder was packed into a stainless-steel pan together with either some amount of electrolyte or none. For TG-DSC analysis, the pan was hermetically sealed. A heat rate of 5^{o}C min^{-1} was set for both TG-DSC and TG-DTA/MS analysis.

Results and Discussion

The synthesized FeOF had been indexed as a tetragonal structure with *$P4_2/mnm$* space group. Figure 1 shows the cycling performances of FeOF cathodes under different cycling depth in Na-ion and Li-ion batteries. A large reversible capacity of 260 mAh g^{-1} was obtained when the electrode was cycled between 4.0 and 0.8 V against Na anodes. Moreover, the FeOF cathode showed relatively good cycling performance over 20 cycles. When the discharge cut-off voltage decreased from 1.0 V to 0.8 V, the largest reversible capacity increased to near 300 mAh g^{-1}. However, rapid capacity fading was observed in the following cycles. On the other hand, FeOF shows relatively good cyclability even for the twice deeper cycle depth against Li. It seems that the volume expansion by the Li insertion is not so serious since the ionic volume of Li is a half of Na.

Figure 2 shows the DSC curves of the electrolyte and the mixture of 1 mg FeOF electrodes with 1 µl electrolyte at different state of charge/discharge. The thermal decomposition of the electrolyte started from 260 ^{o}C. The mixture of cycled electrodes with electrolyte showed less heat generation but much lower onset temperature. The sodiated electrodes showed comparative poorer thermal stability than the desodiated ones. The onset temperatures of the exothermic heat were about 50 ^{o}C lower. Detailed discussion will be presented in the conference.

References

[1] N. Pereira, F. Badway, M.Wartelsky, S. Gunn, and G. G. Amatucci, *J. Electrochem. Soc.*, **156** (2009) A407.
[2] A. Kitajou, R. Nagano, and S. Okada, *Abstract of PRiME2012*, #**851** (2012).

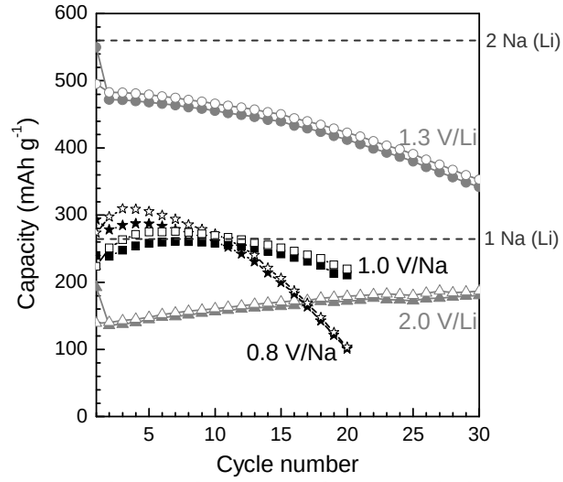

Fig. 1 Cycling performances of FeOF cathodes under different cycling depth in Na-ion and Li-ion batteries. Solid symbols show the discharge capacities, while hollow ones are the charge capacities.

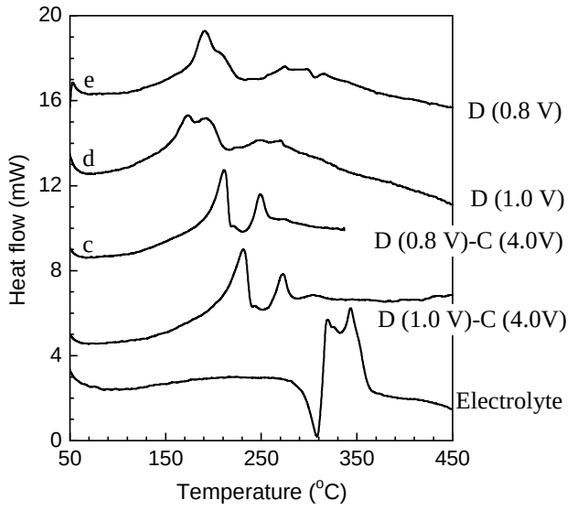

Fig. 2 DSC curves of 1 µl 1 mol cm^{-3} $NaClO_4$/PC and the mixtures of 1 mg cycled FeOF cathodes with 1 µl correlative electrolytes at different state of charge/discharge.