

Kee, Y., Dimov, N., Champet, S., Gregory, D. H., and Okada, S. (0216) Investigation of Al-doping effects on the NaFe0.5Mn0.5O2 cathode for naion batteries. *Ionics*, 22(11), pp. 2245-2248. (doi:<u>10.1007/s11581-016-</u> <u>1839-2</u>)

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Deposited on: 19 September 2016

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# Investigation of Al-doping Effects on the $NaFe_{0.5}Mn_{0.5}O_2$ Cathode Host for Na-ion Batteries

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### Abstract

P2-Na<sub>2/3</sub>MO<sub>2</sub> materials have recently been investigated as promising high-capacity cathode hosts for Na-ion batteries. On the other hand, the Na-deficiency in these materials precludes a high energy density when coupled with Na-free anodes. As an alternative, O3-NaFeO<sub>2</sub> and its various derivatives such as NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> have been suggested and investigated. In this study, we dope Al in NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and investigate Al-doping effects on the electrochemical properties of the Na<sup>+</sup> host. The Al-doped compound shows almost the same conductivity and diffusivity as the pristine structure. However, Al-doping enhances O3-P3 phase transition.

#### Introduction

The reserves of cobalt, which is an essential component of the current high-energy density Li-ion cathodes, are limited and lithium is geographically constrained to several main deposits worldwide. These restrictions have greatly motivated research on Na-ion batteries. As a consequence, there has been a number of studies about Na-ion host compounds based on their well-known Li-equivalents such as NaMPO<sub>4</sub>, Na<sub>3</sub>M<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, and NaMP<sub>2</sub>O<sub>7</sub>. Unfortunately, most of these compounds show significantly inferior electrochemical performance to their Li-equivalents and require further improvement [1, 2, 3]. While Na is the most abundant alkali metal, Fe and Mn are the most widespread transition metals. Thus, Na-Fe-Mn-containing structures could be ideal as low-cost Na<sup>+</sup> electrodes. Among Na-ion host candidates based on Fe and Mn, various Na-deficient P2-type layered Na<sub>2/3</sub>(Fe<sub>y</sub>Mn<sub>1-y</sub>)O<sub>2</sub>

compositions have been investigated as promising high capacity cathode materials, showing energy density only slightly inferior to similar lithium metal oxides [4, 5, 6].

However, these P2-type  $Na_x(M/M')O_2$  phases require an initial discharge capacity that significantly exceeds the initial charge capacity, which makes it difficult for them to be coupled directly with Na-free anodes in sodium-ion batteries regardless of their higher capacity. In such cases, the use of Na-containing anodes would be unavoidable, which is inconvenient and neither a safe nor cost-competitive approach when applied in a mass production process. An alternative is to use O3-type layered NaFeO<sub>2</sub> and its derivatives NaFe<sub>v</sub>Mn<sub>1-v</sub>O<sub>2</sub>. Because these materials are not sodium-deficient, it might be possible to use them as the sole source of Na in a full cell configuration with sodium-free anodes. To the best of our knowledge, the important parameters of NaFe<sub>v</sub>Mn<sub>1-v</sub>O<sub>2</sub> materials such as their diffusivity and electrical conductivity have not been reported so far. On the other hand, the electrochemical performance of NaFe0.5Mn0.5O2 was recently examined against Na and showed large polarization and continuous capacity fading upon cycling [7, 8]. Doping is a common treatment used to improve the electrochemical performance of the electrode hosts. The presence of an electrochemically inactive ion could stabilize the parent structure or facilitate desired phase transitions. The aim of the current study is to explore the effects of Al-doping on NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> as a sodium-ion battery host and to evaluate the diffusivity and electrical conductivity of these materials.

### Experimental

A stoichiometric ratio of the precursors, Fe<sub>2</sub>O<sub>3</sub> (99 %, Sigma-Aldrich), Mn<sub>2</sub>O<sub>3</sub> (99 %, Sigma-Aldrich), Al<sub>2</sub>O<sub>3</sub> (99 %, Sigma-Aldrich), combined with a 10 wt% excess of Na<sub>2</sub>CO<sub>3</sub> (99.8 %, Wako) was ball-milled at 200 rpm for 1 h. The mixture was sintered at 900 °C for 12 h and then sintered again with an intermediate grinding in air. Powder X-ray diffraction (XRD) patterns of NaFe<sub>0.5-x</sub>Mn<sub>0.5-x</sub>Al<sub>2x</sub>O<sub>2</sub> (x = 0 and 0.025) both before and after galvanostatic charging and discharging were recorded *ex-situ* using a Rigaku X-ray powder diffractometer (Cu-K $\alpha$ , 50 kV, 300 mA) over a 2  $\theta$  range of 10-80 ° with a step size of 0.02 ° at a scan rate of 0.2 °/min for the prepared samples. The electrical conductivity of the samples was measured using a powder resistivity measuring system (Mitsubishi Chemical Analytech). The measured volume resistivities are calculated in accordance with equation (1):

$$\rho_{v} [\Omega \text{ cm}] = R [\Omega] \text{ x RCF x t [cm]}$$
(1)

where  $\rho_v$  is the volume resistivity, R is resistance measured by applying Ohm's law, RCF is the automatically calculated Resistivity Correction Factor, and t is sample thickness. BET surface area was obtained from nitrogen adsorption isotherms at 77 K using a Quantachrome Quadrasorb evo instrument with a transducer accuracy of 0.1 % and pressure resolution of 0.016 Torr after vacuum-drying process for 3 h. The working electrodes for galvanostatic charging and discharging were prepared by screen-printing electrode slurries on Al-foil after ball-milling a mixture of electrode active material (70 wt%), acetylene black (25 wt%), and PVDF binder (5 wt%) for 1 h at 500 rpm. The galvanostatic charging and discharging properties for all electrodes were carried out against Na metal using 1 M NaPF<sub>6</sub> in PC:FEC (98 : 2 by volume) as an electrolyte at 0.05 C in the voltage range 2.0-4.0 V. The Galvanostatic Intermittent Titration Technique (GITT) with 10 pulses calculated from the second galvanostatic charging capacity was applied to estimate the diffusivity of each sample.

#### **Results and Discussion**

XRD patterns of the compounds,  $NaFe_{0.5-x}Mn_{0.5-x}Al_{2x}O_2$  (x = 0, 0.025; 1, 2), corresponded to the previously reported pattern for a-NaFeO2 (ICSD #187705) without any distinctive reflections from impurity phases (Fig. 1). The stacking sequence in the layered crystal structure of these compounds classifies them as O3-phases (space group R-3m), while the redistribution of Na<sup>+</sup> ions in the O3-phase upon de-sodiation could result in a P3-phase in which the crystallographic occupancies are altered [9, 10]. The initial charge and discharge performances and the *ex-situ* XRD data for each sample were recorded as illustrated in Fig. 2. In the first cycle, the highest reversible discharge capacity of 125.4 mAh g<sup>-1</sup> was observed from pristine NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, while a slightly decreased discharge capacity of 111.3 mAh  $g^{-1}$ was obtained for NaFe<sub>0.475</sub>Mn<sub>0.475</sub>Al<sub>0.05</sub>O<sub>2</sub>. Heavier Al-doping (e.g. NaFe<sub>0.45</sub>Mn<sub>0.45</sub>Al<sub>0.1</sub>O<sub>2</sub>) resulted in increased polarization and reduced initial discharge capacity. Therefore, only the pristine NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and NaFe<sub>0.475</sub>Mn<sub>0.475</sub>Al<sub>0.05</sub>O<sub>2</sub> samples are considered in this work. However, NaFe<sub>0.475</sub>Mn<sub>0.475</sub>Al<sub>0.05</sub>O<sub>2</sub> showed enhanced capacity retention (82 %) compared to that of NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> (66 %) after the 10th cycle. Most of the layered Na-ion host structures undergo complicated phase transitions upon recharging [8, 10]. It is therefore essential to elucidate the structural effects of doping under various states of charge. The Al-doped material underwent a clear transition to the P3 phase upon charging, while the distinctive reflections of the O3 phase persist upon charging for NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>. Therefore, Al-doping results in somewhat smoother O3-P3 phase transitions upon recharge [12]. Although an improvement in the performance of O3-type NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> has been realized, the Al-doped sample still suffers from continuous capacity fading, which still needs to be further improved to meet industrial needs.

Another notable feature for the examined samples in this study is relatively large polarization even under low current density (C/20). To further analyze the Al-doping effects on diffusion kinetics, Galvanostatic Intermittent Titration Technique (GITT) was performed as illustrated in **Fig.3**. The diffusion coefficient, D, can be estimated from the following equation (2) [11]:

$$D = (4/\pi)(iV_{\rm m}/z_{\rm A}FS)^2[(dE(x)/dx)/(dE/d\sqrt{t})]^2 \quad (2)$$

where *i* (A) is the applied current;  $V_{\rm m}$  (cm<sup>3</sup>/mol) is the molar volume of the electrode material;  $z_{\rm A}$  is the charge number; *F* (C/mol) is the Faraday's constant; *S* (cm<sup>2</sup>) is the electrode/electrolyte interfacial surface area. The  $dE/d\sqrt{t}$  is the voltage versus the square root of the time during constant current pulse, and dE(x)/dx is the slope of the coulometric titration curve, obtained by plotting the equilibrium electrode voltage E(x) against the electrode active material composition after each current pulse. As the electrochemical performance of electrode hosts depends on both the diffusivity of the charge carriers and the electrical conductivity of the host, the electrical conductivity of the samples was measured using a powder resistivity measuring system. **Table 1** lists the calculated diffusivity and electrical conductivity of the samples, showing that Al-doping of the pristine material resulted in only small differences for both electrical conductivity and diffusivity. On the other hand, the total reaction resistance of NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> (648.4 ohm g) was considerably reduced to 530 ohm g in NaFe<sub>0.475</sub>Mn<sub>0.475</sub>Al<sub>0.05</sub>O<sub>2</sub> when Al was introduced as a dopant.

The magnitude of the measured diffusion coefficients is consistent with the observed high polarization even under the low current densities prevalent in this study. Negligible polarization under reasonable current density (*ca.* 1C rate) would be possible only in cases where the characteristic diffusion time ( $\tau$ ), estimated as L<sup>2</sup>/D, is of the order of 1-3 h (3600-10800 s). Therefore, setting  $\tau$ <10000 for L=1 µm determines the desired values of the diffusion coefficient for reasonably fast kinetics. This requires the value of D higher than 10<sup>-12</sup> cm<sup>2</sup>s<sup>-1</sup>. However, the samples showed Na<sup>+</sup> diffusivity that are 5 orders of magnitude lower than this requirement. Attempts to recharge the material at higher rate (ca. 1C) resulted in negligible capacity in accordance with the low diffusivity.

#### **Summary**

In this preliminary research, O3-NaFe<sub>0.5-x</sub>Mn<sub>0.5-x</sub>Al<sub>2x</sub>O<sub>2</sub> (x = 0, 0.025) compounds were synthesized via conventional solid-state reactions and their fundamental properties, Na-ion diffusivity and electrical conductivity, were investigated for the first time. Al-doping on O3-NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> slightly increases the electrical conductivity and Na-ion diffusivity of the parent compound with enhanced P3-O3 phase transition. However, capacity fading is still severe and the kinetics of the electrochemical reaction was not significantly improved. Therefore, the cathode materials based on only the most cost-competitive elements Na, Fe, and Mn with the addition of electrochemically inactive element acting as a structural stabilizer (Al) could not meet the industrial needs for electrochemical performance. However, this result should act as a driving force for the discovery of other M-doped derivatives.

#### Acknowledgments

This work was financially supported by Elements Strategy Initiative for Catalysts and Batteries project, MEXT, Japan.

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## **Table Captions**

**Table1.** The measured electrical conductivity ( $\sigma$ ), Brunauer-Emmet-Teller (BET) specific surface area (SSA), and Na<sup>+</sup> diffusion coefficient (D) of each sample.

# **Figure Captions**

Fig. 1 XRD patterns of (a)  $\alpha$ -NaFeO<sub>2</sub> (ICSD #187705), (b) as-synthesized NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, and (c) as-synthesized NaFe<sub>0.475</sub>Mn<sub>0.475</sub>Al<sub>0.05</sub>O<sub>2</sub>.

Fig. 2 Electrochemical performance of NaFe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> (1) and NaFe<sub>0.475</sub>Mn<sub>0.475</sub>Al<sub>0.05</sub>O<sub>2</sub> (2): *Ex-situ* XRD patterns of (a) pristine 1, (d) pristine 2, (b) 1 after charging, (e) 2 after charging, (c) 1 after discharging and (f) 2 after discharging. Black circles indicate the most distinctive low-angle peaks attributable to the P3 phase.

**Fig. 3** The GITT plots for (a)  $NaFe_{0.5}Mn_{0.5}O_2$ , and (b)  $NaFe_{0.475}Mn_{0.475}Al_{0.05}O_2$ . The reaction resistance of each sample was calculated by dividing the overpotential of each pulse by the applied current (C/20).

Table	1.

	$\sigma$ (S cm <sup>-1</sup> )	$SSA (m^2 g^{-1})$	$D (cm^2 s^{-1})$
NaFe <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>2</sub>	5.154x10 <sup>-5</sup>	1.049	$2.409 \times 10^{-17}$
NaFe <sub>0.475</sub> Mn <sub>0.475</sub> Al <sub>0.05</sub> O <sub>2</sub>	$5.696 \times 10^{-5}$	1.985	$3.414 \times 10^{-17}$



Fig. 1



Fig. 2



Fig. 3