



## Microstructure design of metal composite for active material in sodium nickel-iron chloride battery



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### HIGHLIGHTS

- The disconnection of Ni networks frequently occurs in a Na-NiCl<sub>2</sub> battery.
- The disconnection is reduced by the microstructure design of active materials.
- The electrochemical potential and particle size must be considered.
- The cycle performance is dramatically improved by the microstructure design.

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### ABSTRACT

In this manuscript, it is reported how the microstructure of metal composites can be designed to obtain excellent cycle performance in Na-(Ni,Fe)Cl<sub>2</sub> battery. The microstructure consists of an active material and a conducting material. The conducting material is an active material as well as a conducting chain (an electron path). In Na-(Ni,Fe)Cl<sub>2</sub> cells, it is preferable that Ni is selected as the conducting material, since the nickel chloride is not formed on the surface of Ni particles during the electrochemical reaction of Fe particles. In addition, the particle size of Ni should be smaller than that of Fe, in order to ensure that the conducting chain is well-connected. Through this design, the cycle performance of a Na-(Ni,Fe)Cl<sub>2</sub> cell was significantly improved, compared to that of a Na-NiCl<sub>2</sub> cell. At the 100th cycle, the charge/discharge capacity of a Na-(Ni,Fe)Cl<sub>2</sub> cell was much higher than that of a Na-NiCl<sub>2</sub> cell, approximately 42%.

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### 1. Introduction

Energy storage system (ESS) has gained considerable attention owing to environmental concerns over the use of fossil fuels and their resource constraints. Li-ion battery has been considered as a candidate of ESS, because of the high energy density. However, the Li-ion battery has been concerned about the safety, cost, and size issues. Therefore, recently, new ESSs have been studied as alternatives to Li-ion batteries. Among the new ESSs, Na-NiCl<sub>2</sub> battery

has emerged as one of the obvious candidates, since it has a lot of advantages such as high safety, low cost, large scale etc. [1–22]. Nevertheless, recently, the development of cheap metal additives have been additionally required in Na-(Ni,M)Cl<sub>2</sub> cells [M: a metal additive]. It is due to the intense price competition in ESS. Until now, Fe has been a representative additive [3–14,22].

In Na-NiCl<sub>2</sub> cell and Na-(Ni,M)Cl<sub>2</sub> cells, there are several factors which are critical to the electrochemical performance, such as the high conductivity of a β"-alumina solid electrolyte (BASE) tube and the reliable microstructure of a cathode layer [3–18]. Among these factors, the microstructure must be designed to have high electronic/ionic conductivity in a cathode layer [3,12,15]. High ionic conductivity depends on the quality of the 2nd electrolyte and the porosity of the composite which consists of active metals and NaCl.

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Since the 2nd electrolyte is liquid at the working temperature (approximately 300 °C), the ionic conductivity depends on the porosity of the composite (active materials + NaCl). On the other hand, the electronic conductivity is dependent on the microstructure of metal chains, which must have dependable connectivity in a cathode layer as shown in Fig. 1(a). Hence, the microstructure studies of Ni particles have been conducted in a Na-NiCl<sub>2</sub> cell [15]. However, they have not been reported in Na-(Ni,M)Cl<sub>2</sub> cells.

This study proposes a method for designing the microstructure of metal composites to have dependable connectivity in a cathode layer, in order to obtain excellent cycle performance in Na-(Ni,M)Cl<sub>2</sub> cells. In addition, Na-(Ni,Fe)Cl<sub>2</sub> cells were prepared and their electrochemical behaviors were investigated to confirm the microstructure design of the metal composites.

## 2. Microstructure design of metal composites

In order to obtain the reliable connection of conducting chain, the formation of a metal chloride must be minimized as shown in Fig. 2. This is due to the effect of a metal chloride on the disconnection of conducting chain as shown in Fig. 2(a). The formation of a metal chloride can be minimized by the microstructure design of metal composites in Na-(Ni,M)Cl<sub>2</sub> cells. The composite of Ni and a metal additive (metal composite) must be prepared, taking into consideration the electrochemical potential of a metal additive as shown in Fig. 1(b), in order to maintain the connectivity of conducting chains during the electrochemical reaction of Na-(Ni,M)Cl<sub>2</sub> cells. Namely, the conducting chains must be formed by the metal particles which have relatively high electrochemical potential between Ni and a metal additive as indicated in Fig. 2(b)–(c).

Fig. 2(a) shows the formation of NiCl<sub>2</sub> on the surface of Ni particles and the charge/discharge behavior of Ni particles in a Na-NiCl<sub>2</sub> cell. As seen in this figure, the disconnection of Ni chains can occur owing to the thick NiCl<sub>2</sub> layer, which is formed on the surface of Ni particles in a Na-NiCl<sub>2</sub> cell. The thickness of the NiCl<sub>2</sub> layer can be reduced when a metal additive is added as shown in Fig. 2(b)–(c), since the metal additive consumes a portion of Cl<sup>-</sup> ions at the charge reaction. During the charge reaction of Fe, the NiCl<sub>2</sub> layer is not formed on the surface of Ni particles as shown in Fig. 2(b). Thus, the addition of a metal additive reduces the thickness of NiCl<sub>2</sub> layers. In particular, the conducting chains must be formed by Ni particles in Case I, as shown in Figs. 1(b) and 2(b), since pure Ni chains can be used for the conducting chains in the charge/discharge reaction of a metal additive. On the contrary, when the

electrochemical potential of a metal additive is higher than Ni (Case II), the metal additive must form the conducting chains as seen in Fig. 2(c).

In order to confirm this concept, Fe was chosen as the metal additive. The Na-(Ni,Fe)Cl<sub>2</sub> cell corresponds to Case I (Fe: 2.35 V, Ni: 2.58 V, at the electrochemical potential). Therefore, the particle size of Fe (6.5 μm, in this study) is required to be larger than that of Ni (2.5 μm, in this study) as shown in Fig. 3. The conducting chains must be formed by Ni particles in Case I. The microstructure of this metal composite (Ni + Fe) can be controlled by the weight ratio between Ni particles and Fe particles as indicated in Fig. 3. If the surface coverage is higher than 100% (region 1), it means that Ni particles are more than enough to cover the surface of Fe particles. On the contrary, “Region 2” means that the Ni particles cannot completely cover the surface of the Fe particles as seen in Fig. 3. 0.9/0.1 and 0.8/0.2 (Ni/Fe, weight ratio) composites are located in Region 1, while a 0.6/0.4 composite belongs to Region 2.

## 3. Experimental

The NaAlCl<sub>4</sub> was synthesized at 300 °C, using NaCl (98%, Sigma Aldrich) and AlCl<sub>3</sub> (99.985%, Alfa Aesar) powders. Sulphur powder (Sigma Aldrich) was added to the NaAlCl<sub>4</sub> powder (approximately 5 wt%). It was used to remove the oxide layers from the surface of metal particles (Ni and Fe) [20,21]. The cathode layer was prepared using Ni (99.7%, 2.5 μm, Standard Grade, Vale), Fe (99.5%, 6.5 μm, International Specialty Products), NaCl, and S-added NaAlCl<sub>4</sub> (the 2nd electrolyte) powders. The weight ratio between NaCl powder and Ni + Fe powders was 2.0 [(Ni + Fe)/NaCl = 2.0 g/1.0 g]. Various mixtures of Ni and Fe powders were used, such as Ni/Fe = 1.0/0, 0.9/0.1, 0.8/0.2, and 0.6/0.4 (weight ratio). Thus, the theoretical capacity of the cells is approximately 230–235 mAh g<sup>-1</sup> (per the weight of Ni and Ni-Fe particles). The microstructures of prepared powders and cells were observed using a scanning electron microscope (SEM, JSM-5800; JEOL CO., Tokyo, Japan). The surface of the β"-alumina solid electrolyte (BASE; Ionotec, UK) tube was covered with carbon paste and heat-treated at 230 °C for 30 min. The cells were cycled at 300 °C (between 2.2 V and 2.8 V, at the rate of C/9) in an argon-filled glove box, using VMP3 (Bio Logic SAS, France).

## 4. Results and discussion

Fig. 4 shows the microstructures of Ni-Fe composites and a 0.6/0.4 cell. As seen in Fig. 4(a), the sizes of agglomerated Ni and Fe

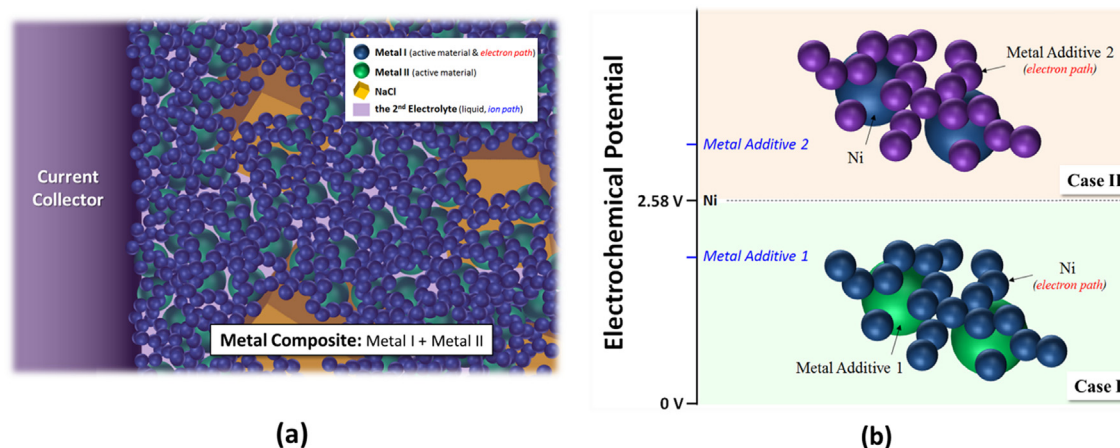


Fig. 1. Microstructure of (a) cathode layer and (b) metal composites: In Case I, the electrochemical potential of metal additive 1 is lower than that of Ni. The potential of metal additive 2 is higher than that of Ni in Case II. The metal chain (electron path) must be formed by Ni in Case I and metal additive 2 in Case II.

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