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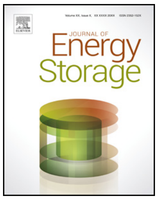

Synthesis and characterization of $Na_2Ti_6O_{13}$ and $Na_2Ti_6O_{13}/Na_2Ti_3O_7$ sodium titanates with nanorod-like structure as negative electrode materials for sodium-ion batteries

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ABSTRACT

In this work, we report microwave assisted hydrothermal synthesis of monoclinic sodium titanates with either tunnel or with mixed tunnel/layered structure. Single phase $Na_2Ti_6O_{13}$ and mixed phase $Na_2Ti_6O_{13}/Na_2Ti_3O_7$ titanates were studied by electrochemical measurements with cyclic voltammetry, impedance spectroscopy and galvanostatic cycling. SEM images revealed that all the synthesized materials consist of rods with widths in the range of tenths to hundreds nanometers. XRD analysis was used for determination of the phase composition and crystallite size.

It was shown that mixed phase electrode material reveals higher capacity and wider active voltage range but has also lower cycling stability. The insertion potential of layered titanate $Na_2Ti_3O_7$ is much lower than in the case of $Na_2Ti_6O_9$ and the specific capacity of mixed titanate in the first cycle is double the capacity of pure $Na_2Ti_6O_9$. Although presence of layered titanate contributed to high specific capacity in early cycling, it allowed a considerable decrease in specific capacity at higher numbers of cycles.

1. Introduction

Sodium-ion batteries attract significant attention of researchers worldwide and the number of published papers grows rapidly since 2012. Fig. 1 shows that while less than 20 relevant articles appeared in 2011; already more than 600 were released in 2016. The rising interest in the topic follows especially from the growing demand for lithium-ion batteries caused by electromobility having become more reasonable and available. The price of pure lithium carbonate as the most vital precursor for the active electrode materials employed in lithium-ion batteries far surpassed its previous historical maximum at the beginning of 2016 [1]. Such an increase is ascribed to the expected massive surge in the production of Li-ion batteries for electric vehicles. Sodium-ion batteries embody very promising power source to complement lithium-ion ones, mainly because they utilize the same principles and technology. At the cost of lower energy density, the former type can potentially provide for a solid energy storage system without the need of the rarer elements, lithium in particular. Sodium is an abundant element, occupying 2.6% of the Earth's crust, and is very easy to obtain.

Despite the considerable similarity in sodium and lithium properties, previous experiments have shown that the key intercalating hosts which interact well with lithium ions usually do not exhibit the same good properties in relation to intercalation of sodium.

The most conspicuous example of the diverse behavioral patterns characterizing the intercalation of lithium and sodium consist in the interaction with graphite, a material commonly used as an active material of lithium-ion battery anodes but inapplicable for sodium-ion cells. On the other hand, using layered oxides as intercalation hosts, sodium due to its larger ionic radius, does not tend to mix with the transition metal in the host. Moreover, it was theoretically calculated that in most ceramic layered intercalation materials, Na^+ ion migration barrier is similar to (and may even be lower than) the corresponding Li^+ migration barriers. On the other hand, significantly higher Na^+ diffusion barrier was found for a tunnel structure of spinel materials, as was demonstrated on an $AFePO_4$ compound.

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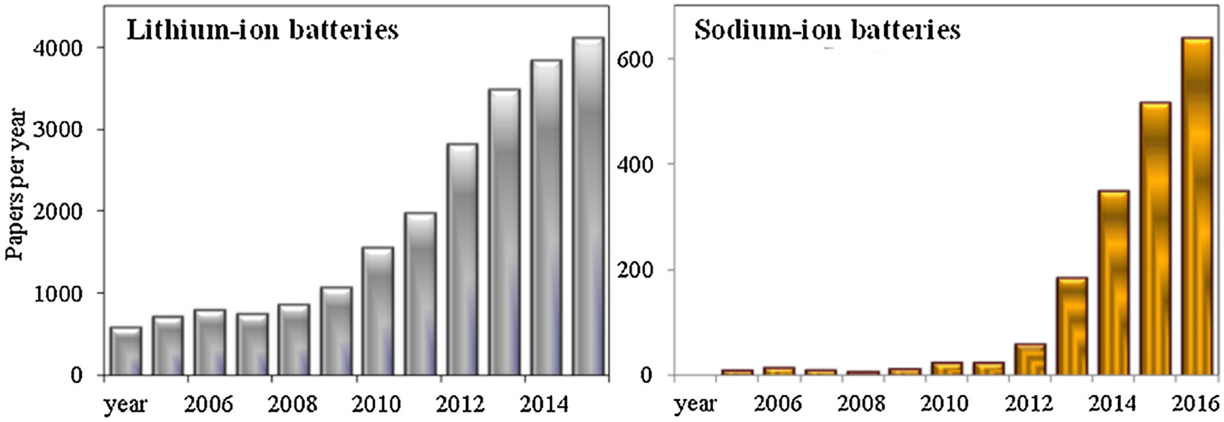

Fig. 1. The scientometric data related to articles published in the domain of lithium and sodium ion batteries.

Due to the low reactivity of the titanium oxide compound and the ability to find candidates with good electrochemical stability, the research efforts the given field are particularly suited for identifying a stable titanium material having a redox potential as low as possible, together with sufficient capacity retention.

Layered and tunnel structure titanium oxide materials have been intensively studied in the domain of lithium-ion batteries; in particular, lithium pentatitanate $Li_4Ti_5O_{12}$ exhibit very favorable cycling stability due to its low volume changes during process. The high stability, however, is achieved at the expense of high redox potential accompanying lithium insertion, and thus also low full-cell voltage. Recently, titanium oxide based materials have been extensively examined also as sodium ion hosts. $Li_4Ti_5O_{12}$ was reported as a sodium ion intercalation host [2–4] with a good cycling performance and specific capacities in the range of between 140 mAh/g–180 mAh/g. A novel layered type of sodium titanate $NaTi_3O_6(OH)\cdot 2H_2O$, was studied by Shirpour [5], who focused on both the hydrated and the dehydrated forms; besides, considerable first cycle irreversible capacity shows the interesting result of 120 mAh/g in the initial 20 cycles.

Sodium titanates are relatively wide group of compounds where change in the stoichiometric ratio of sodium to titanate changes the crystallographic structure and thus allows obtaining not only a layered but also a tunnel structure. The $NaTiO_2$ material was reported for lithium-ion storage, ensuring the reversible charge capacity of 152 mAhg^{-1} when cycled at the current densities of 0.1C [6]. It was also shown by an in-situ X-ray diffraction that electrochemical sodiation and desodiation of $NaTiO_2$ changes its lattice structure from monoclinic to hexagonal. The sodium storage behavior of $Na_2Ti_7O_{12}$ nanowires grown in situ on a titanium mesh substrate was studied by Li et al. showing the capacity of 258 mA h g^{-1} at 0.1C; the mass loading corresponded to 2 mg cm^{-1} with the irreversible capacity amounting to 50% in the first cycle. There are two forms of sodium titanates which can be prepared simultaneously and the ratio of the two phases can be tuned just by slightly changing the sodium content in the precursor mixture – the sodium hexatitanate $Na_2Ti_6O_{13}$ and sodium trititanate $Na_2Ti_3O_7$. Synergistic effect on performance of such mixture utilized as an electroactive material for sodium-ion cells was demonstrated by Ho et al. [7]. Fig. 2 shows the structure of these two modifications of sodium titanates widely studied both for the lithium-ion and the sodium-ion batteries. While the investigation of lithium insertion in the structures of these ceramic materials was already performed very broadly in the last decade [8–12], most of the contributions discussing with sodium insertion into these two structural forms were published only in the last two years [13,8,14–18].

2. Experiment

2.1. Preparation of nanostructured sodium titanates

A well crystalline $Na_2Ti_6O_{13}$ and mixed $Na_2Ti_6O_{13}/Na_2Ti_3O_7$ samples were obtained via calcination of microwave assisted hydrothermally synthesized precipitate, where titanium isopropoxide TiPr (CAS 546-68-9), sodium hydroxide NaOH and hydrogen peroxide H_2O_2 were used as precursors. All the chemicals were purchased from Sigma-Aldrich. The general preparation procedure comprised mixing a 2,5 M aqueous solution of NaOH with 30% solution of hydrogen peroxide, with the subsequent addition of titanium isopropoxide (TiPr). Thus, two samples were prepared, differing in the molar ratio of Na/Ti. The molar ratio of 1/3 leads to pure hexatitanate $Na_2Ti_6O_{13}$ and the molar ratio of 3/2 produces

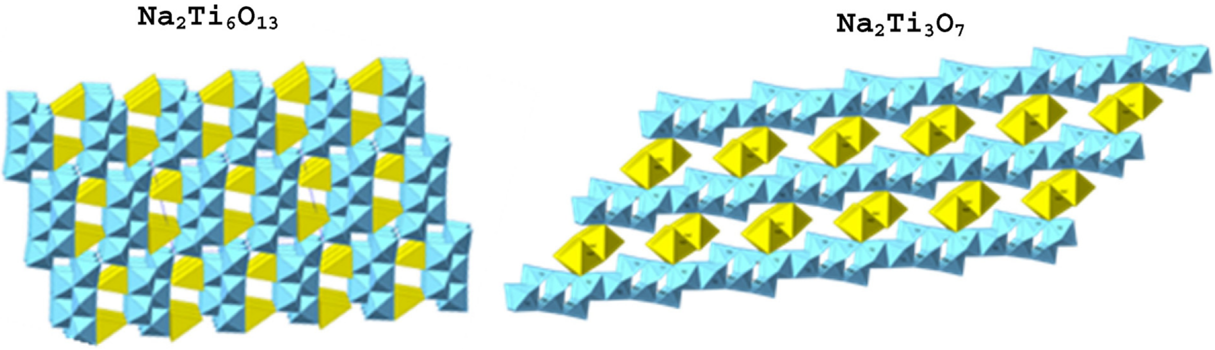

Fig. 2. The visualized tunnel structure of hexatitanate $Na_2Ti_6O_{13}$ (left) and layered structure of trititanate $Na_2Ti_3O_7$ (right).

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