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High-rate intercalation capability of $NaTi_2(PO_4)_3$/C composite in aqueous lithium and sodium nitrate solutions

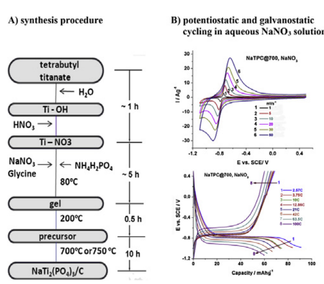
Milica Vujković [a], Miodrag Mitrić [b], Slavko Mentus [a, c, *]

[a] University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12-16, 11158 Belgrade, Serbia
[b] University of Belgrade, Vinča Institute of Nuclear Sciences, Laboratory for Theoretical and Condensed Matter Physics, 11001 Vinča, Serbia
[c] Serbian Academy of Sciences and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia

HIGHLIGHTS

- $NaTi_2(PO_4)_3$/C composite was synthesized by gel-combustion procedure.
- Intercalation kinetics was investigated in aqueous nitrate solutions.
- Very fast intercalation/deintercalation kinetics was observed.
- Ohmic type of current–voltage dependence observed by cyclic voltammetry.
- Suprisingly low dependence of capacity on the intercalation rate up to 100C.

GRAPHICAL ABSTRACT



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ABSTRACT

The nanodispersed $NaTi_2(PO_4)_3$/C composite containing 20–25 wt.% of in-situ formed carbon, was synthesized by gel combustion procedure followed by a heat treatment at 650, 700 and 750 °C. The samples calcined at 700 and 750 °C displayed crystalline nasicon structure. They were subjected to the investigation of intercalation/deintercalation kinetics in aqueous $NaNO_3$ and $LiNO_3$ solutions, using cyclic voltammetry and galvanostatic charging/discharging measurements. As regards to the effect of electrolyte composition, the reactions were evidenced to be roughly twice faster in sodium nitrate than in lithium nitrate solution. Among the samples treated at 700 and 750 °C, better performance was evidenced for the sample treated at lower temperature. Coulombic capacity in $NaNO_3$ solution at charging rate 1C amounted to ~70 mAh g^{-1} and ~55 mAh g^{-1} for the sample calcined at 700 and 750 °C, respectively, and displayed surprisingly slight dependence on charging rate up to even 100C.

1. Introduction

Sodium rechargeable batteries (SRB) became a real alternative to lithium rechargeable batteries, thanks not only to the closeness in energy and power characteristics, but also to both higher abundance and significantly lower price of sodium minerals [1–7]. The recent studies on SRB are summarized in several review papers [8–12]. The investigations of sodium aqueous rechargeable batteries (ARSB) [6,13–23] present an accompanying research area, interesting from the viewpoint of environmental friendliness, safety and simple production. The high capacity and excellent reversibility during sodiation/desodiation cycling has been already achieved for different electrode materials in both organic

* Corresponding author. University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12-16, 11158 Belgrade, Serbia.
E-mail address: slavko@ffh.bg.ac.rs (S. Mentus).

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[1,3,4,24–26] and aqueous electrolyte solutions [6,13–23].

$LiTi_2(PO_4)_3$ was shown to be suitable anode materials for aqueous Li-ion batteries [27–29]. According to the former structure investigation [30,31], Nasicon-type $LiTi_2(PO_4)_3$, consisted of TiO_6 octahedra corner-shared with PO_4 tetrahedra. In this compound, the Li^+ ions were placed in octahedral M1 sites (single available per formula unit), while tatrahedral M2 sites (three ones available per formula unit) are empty. $LiTi_2(PO_4)_3$ may reversibly inset two lithium ions, on account of the Ti^{4+}/Ti^{3+} reduction, according to a two-phase equilibrium mechanism between $LiTi_2(PO_4)_3$ and $Li_3Ti_2(PO_4)_3$ along a flat insertion plateau [32,33]. During the electrochemical transformation $LiTi_2(PO_4)_3 \rightarrow Li_3Ti_2(PO_4)_3$, inserted Li^+ ions accommodate in M2 sites [32]. The recent refined structure investigations performed by Aatiq et al. [33] evidenced that in $Li_3Ti_2(PO_4)_3$ the positions occupied during intercalation are not exactly M2, but, somewhat displaced, M3′ and M3″ ones, accepting 2/3 and 1/3 of intercalated Li^+ ions, respectively. During the lithiation, no change in lattice parameters of either initial $LiTi_2(PO_4)_3$ (space group $R\overline{3}C$), ($a = 8.508(1)$ Å, $c = 20.833(6)$ Å) or final $Li_3Ti_2(PO_4)_3$ (space group $R\overline{3}$), $a = 8.390(1)$ Å, $c = 22.886(2)$ Å) were detected by XRD analysis [34].

Nasicon type compound $NaTi_2(PO_4)_3$ has been known long time ago, however, his intercalation behavior appeared initially not enough attractive [35,36]. After the prediction of lower barrier for diffusion of Na^+ ions relative to Li^+ ions for open layer Nasicon structures [37,38], $NaTi_2(PO_4)_3$ became interesting as an intercalation material. Different methods of synthesis were reported for nasicon-type $NaTi_2(PO_4)_3$ including high- [18,30,31,39,40] and low temperature [41,42] solid–state reactions, sol–gel [42], hydrothermal [43], microwave [44] or Pechini [16] methods.

According to the structure investigation reported in the literature [30,31], nasicon-type $NaTi_2(PO_4)_3$ is isostructural with $LiTi_2(PO_4)_3$, with M1 sites completely occupied by Na^+ ions and M2 sites empty. The reversible sodiation of $NaTi_2(PO_4)_3$ in organic electrolyte solutions was first time reported by Delmas et al. [30,31], who showed that two additional sodium ions could be reversibly intercalated on account of the Ti^{4+}/Ti^{3+} redox reaction. The theoretical coulombic capacity corresponding to this extent of intercalation was calculated to amount to 133 mAh g^{-1}. Park et al. [16] investigated the electrochemical behavior of $NaTi_2(PO_4)_3$ (obtained by Pechini method) in both organic and aqueous electrolytes, and evidenced improved kinetics of sodiation/desodiation, particularly in aqueous electrolyte solutions, on account of increase of sample conductivity. A high initial discharge capacity of 123 mAh g^{-1} found in Na_2SO_4, decreased after 30 cycles to approx. 70 mAh g^{-1}. Low equilibrium potential of Ti^{4+}/Ti^{3+} redox pair in aqueous electrolyte (~−0.8 V vs Ag/AgCl) [16], make him a very attractive anode material of aqueous Na-ion batteries. Senguttuvan et al. [45] published the detailed structure investigation during the electrochemical transition $NaTi_2(PO_4)_3 \rightarrow Na_3Ti_2(PO_4)_3$ where the authors confirmed that the intercalated Na^+ ions accommodate in M2 positions. Kabbour et al. [46] determined the structure of ordered α-$Na_3Ti_2(PO_4)_3$ in which 1/3 of the present Na^+ ions occupy all available M1 positions, while remaining 2/3 ions occupy M2 positions.

Recently, Wu et al. [18] synthesized $NaTi_2(PO_4)_3$/C composite by a high temperature reaction. They combined $NaTi_2(PO_4)_3$/C as anode material with $Na_2NiFe(CN)_6$/C as cathode material forming an aqueous Na-ion battery with an acceptable rate capability and cycling stability in aqueous Na_2SO_4 solution. This battery was cycled at the rates up to 5C, and after 250 cycles delivered a coulombic capacity of 79 mAh g^{-1} (being 88% of the initial capacity). Favorable behavior of aqueous batteries composed of $NaTi_2(PO_4)_3$/C based anode materials and $Na_{0.4}MnO_2$ cathode in sodium sulfate solutions were also reported [19,20,22,23].

Patoux et al. [34,47], dealing with the organic electrolyte solutions, demonstrated the feasibility of electrochemical lithiation of $NaTi_2(PO_4)_3$ and investigated structural changes during its both lithiation and sodiation, however, the same was not performed in aqueous electrolytes. The thermodynamic aspect of sodiation of $NaTi_2(PO_4)_3$ in aqueous solutions was reported [16]. In several recent studies, also very promising rate performance of $NaTi_2(PO_4)_3$ in aqueous Na_2SO_4 solutions was reported [19–23].

The main intention of this study was to provide informations about the intercalation rate capability of $NaTi_2(PO_4)_3$ in aqueous nitrate solutions with respect to both lithiation and sodiation, since lithium nitrate was often used in intercalation tests in aqueous solution. For the synthesis of $NaTi_2(PO_4)_3$/C composite, we used simple glycine/nitrate gel combustion method. The obtained raw powder was heated isothermally at 650, 700 and 750 °C in inert atmosphere, in order to examine the effect of temperature on the structure and the kinetics of intercalation reactions. While the sample treated at 650 °C remained amorphous, the powders treated at 700 and 750 °C displayed nasicon-type structure. Only crystalline products displayed intercalation capability, and they were subjected to detailed electrochemical investigations. The intercalation rate performances were found to depend on both solution composition and treatment temperature. The clue finding are that these composite materials displayed very fast intercalation and deintercalation reactions, and the coulombic capacity displayed very slight dependence on the process rate.

2. Experimental

2.1. Sample preparation

Nasicon-type $NaTi_2(PO_4)_3$/C composite (NaTPC) with in-situ incorporated carbon was prepared by the gel combustion process followed by calcination, according to the scheme presented in Fig. 1. Firstly, titanyl hydroxide [$TiO(OH)_2$], obtained by hydrolysis of tetrabutyl titanate [$Ti(C_4H_9O)_4$] (Merck, p.a) under ice-cold condition and constant stirring, was converted to titanyl nitrate

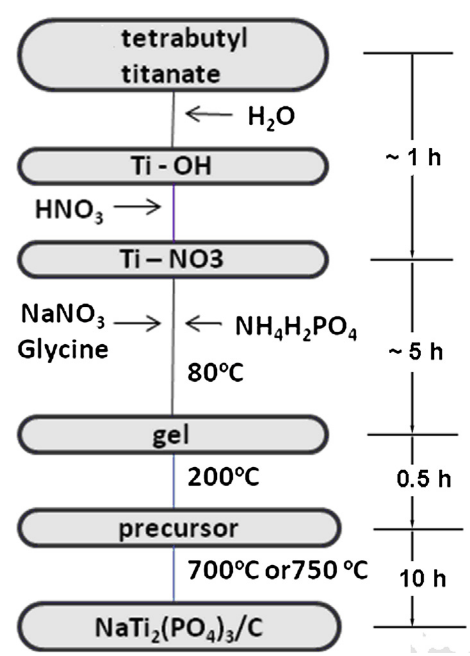

Fig. 1. Schematic representation of the gel-combustion synthesis procedure of $NaTi_2(PO_4)_3$/C composite.