

# Sodium Titanate for Sodium-Ion Batteries<sup>1</sup>

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**Abstract**—First research related to the intercalation of sodium atoms into the structure of the host material emerged in the early 1980s. Since that time, the development of sodium-ion batteries continues. In the last decade, a considerable attention is aimed at sodium-ion batteries with the context of renewable energy sources. The consumption of non-renewable resources like oil or coal resulted in an increasing problem related to the production of greenhouse gases. The main solution to this problem is the generation of energy by renewable energy sources like wind, sun, or hydropower. Solar and wind energies are among non-dispatchable energy sources, i.e. the energy cannot be dispatched at a request of the power grid or the plant owner according to current needs. Renewable energy sources need energy storage devices for energy accumulation. Batteries play a crucial role in that application. Sodium-ion batteries present a promising solution that can deliver low-cost, environmentally friendly energy storage for sustainable development of the human society. This manuscript provides a brief introduction into the field of sodium-ion batteries and describes a simple preparation method of a negative electrode material for sodium-ion batteries that is based on sodium-titanate ceramics—NaTiO.

**Keywords:** accumulation, sodium, battery, capacity, renewable energy, negative electrode

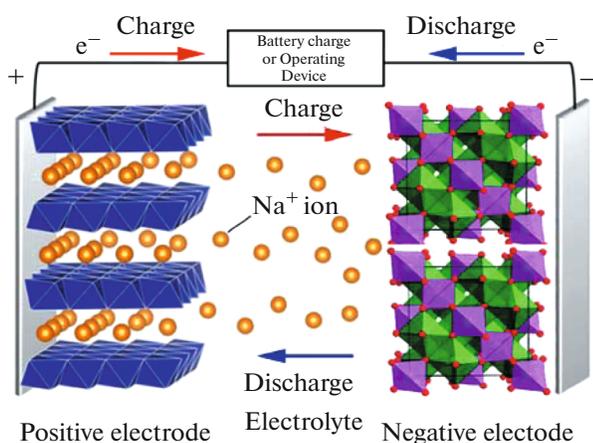
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## 1. INTRODUCTION

Lithium, thanks to its chemical and physical properties, became one of the most important elements in the field of electrochemical energy storage. Lithium is the lightest known metal and it has the smallest atoms (diameter 3.34 Å) of all alkali metals. Lithium possesses one electron in the outermost shell and it ensures a one-electron process that provides a single flat working potential plateau. Using lithium atoms (lithium ions) as charge transfer elements turned out to be a correct way for a new battery generation. Lithium has interesting electrochemical properties related to its intercalation capabilities into various hosts, with different crystal structures layered, olivine or spinel. Lithium-ion batteries (LIBs) have had a long development way since their commercial release in 1991; today they are the most used type of batteries. LIBs have a wide range of applications from small batteries in portable devices, through high power applications in electric vehicles, up to large volume and capacity stationary storage systems connected to the grid and renewable energy sources (photo-voltaic or wind

power). Along with the growth of human society, growing demands to energy and sustainable development with respect to the environment, another electrochemical storage is needed. The main requirements for the new generation of energy storage systems are low cost and environmentally friendly. Sodium-ion batteries (SIBs) belong to the group of so-called post-lithium systems along with lithium-oxygen (air) and lithium-sulphur systems. SIBs have a lot in common with LIBs: a similar operation principle (rocking chair), electrode materials work on insertion or intercalation reaction or using aprotic electrolytes (see Fig. 1) [1–8]. The SIBs have one important advantage—sodium, the sixth most abundant element in the earth's crust. Its annual production is over 255 million tons, in contrast to lithium, which has an enhanced annual production of around 0.045 million tons. Sodium seems to be a promising replacement for lithium. It is the second lightest metal and possesses only one electron in the outermost shell. However, there are some differences between sodium and lithium atoms. Sodium atoms are bigger, heavier, and have a higher standard electrode potential (SHE) than lithium. Sodium atom diameter is 3.8 Å along with a higher atomic mass 22.98 g/mol (lithium 6.94 g/mol),

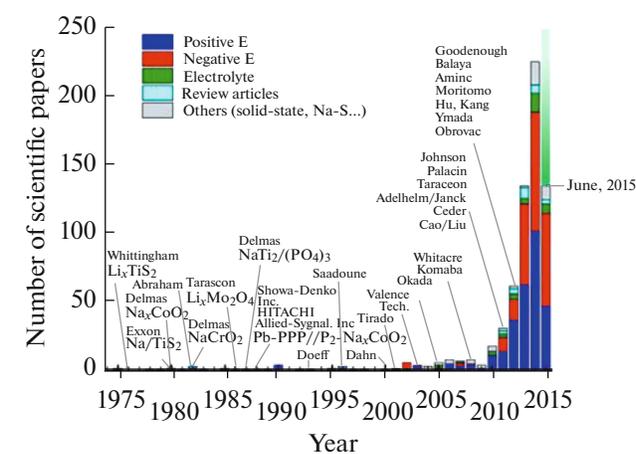
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**Fig. 1.** Schematic illustration of SIBs operation principle. Positive electrode is layered oxide material; negative one is of spinel structure material [1].

electrode potential vs. SHE for sodium is  $-2.71$  V (lithium  $-3.02$  V). Thus, sodium is determined to have lower power and energy density than lithium. Despite that, sodium is due to its natural occurrence and non-toxicity one of the most promising elements for next generations of batteries [9–16].

The LIBs and SIBs technology, components used, and manufacturing processes are very similar. The main concept of SIBs is the usage of an aprotic organic electrolyte based on ester or ether polar solvents like dimethyl carbonate, ethylene carbonate, or propylene carbonate. Mixtures of those solvents can ensure sufficient chemical, electrochemical and thermal stability with a large working potential window. Sodium salts represent analogy to lithium salts used in LIBs. Sodium perchlorate ( $\text{NaClO}_4$ ), parallel to lithium perchlorate ( $\text{LiClO}_4$ ) and sodium hexafluorophosphate ( $\text{NaPF}_6$ ), similar to lithium hexafluorophosphate ( $\text{LiPF}_6$ ), belong to the main sodium salts used in SIBs. As in the case of sodium salts, the situation around cathode (positive electrode) materials for SIBs is analogical to the common cathode materials used in LIBs. LIBs typically use lithium cobalt oxide ( $\text{Li}_x\text{Co}_y\text{O}_2$ ), lithium nickel manganese oxide ( $\text{LiNi}_x\text{Mn}_y\text{O}_2$ ) or lithium iron phosphate ( $\text{NaPF}_6$ ) as cathode material. For SIBs, analogical materials with similar crystal structure and electrochemical behavior can be found. These materials allow the reverse insertion or intercalation of sodium atoms. Cathode materials for SIBs possess similar capacity (mAh/g) and working potential ( $E$  vs.  $\text{Na}/\text{Na}^+$ ) as their lithium counterparts. In the case of the anode (negative electrode) material for SIBs, the situation is not as clear and straight as in the previous examples. Due to the diameter of sodium atoms (sodium atoms are larger than the lithium ones), the insertion of sodium atoms among graphite



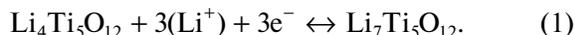
**Fig. 2.** Number of publications, related to sodium for energy storage devices, published in the past three decades. Source: Web of Science, Thomson Reuters [1].

sheets does not occur. The distance between graphite sheets is in the case of natural graphite  $3.34$  Å and does not allow entering of sodium atoms. Therefore, an intensive research effort to find a suitable host for sodium atoms is being done [17–20]. There are many possibilities, like carbonaceous materials (hard and soft carbon), metal alloys, or metal oxides. Hard and soft carbon exhibits sufficient capacity with a low voltage working potential, but huge irreversible capacity of these materials and the cycle stability is still a challenge. Metal alloys like sodium or silicon tin ( $\text{Na}/\text{Si}_x\text{Sn}_y$ ) provide superior capacities (thousands mAh per gram of an active electrode material) but their volumetric changes and instability limit these materials. Another group of electrode materials—metal oxides, represents a challenging mix of the previous electrode material group. They combine good capacity, stability, material accessibility along with an acceptable working potential plateau. Metal oxides already exist and are commercially used in LIBs. Approximately 4% of all manufactured LIBs have negative electrodes made from lithium titanate oxide ( $\text{LiTiO}$ ). This spinel structure material exhibits high cyclability and stability, together with relatively high working potential. Similar to  $\text{LiTiO}$ , there is also  $\text{NaTiO}$  (sodium titanate oxide). This material seems to be a promising candidate for negative electrodes in SIBs. The research effort related to SIBs, represented by number of publications, is shown in Fig. 2 below [21–34].

## 2. EXPERIMENTAL

As a promising anode (negative electrode) material for SIBs, sodium titanate oxide ( $\text{Na}_x\text{Ti}_y\text{O}_z$ ) was synthesized and electrochemically tested in a half cell arrangement. The goal was to obtain a material with similar, or the same, crystal structure, morphology

and properties as lithium titanate oxide (LTO) with formula  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . The equation describing a half-cell reaction is shown below (see Eq. (1)). Theoretical capacity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  calculated with the help of Faraday's law of electrolysis is 175 mAh/g



The prepared  $\text{Na}_x\text{Ti}_y\text{O}_z$  underwent a number of analytical tests. The phase composition, micro-morphology and elemental analysis of the compound were characterized by the X-ray diffraction (XRD), the scanning electron microscopy (SEM), and the energy dispersive spectroscopy (EDS), respectively. Finally, electrochemical testing was performed on a selected sample of sodium titanate.

### 2.1. Synthesis

The  $\text{Na}_x\text{Ti}_y\text{O}_z$  material was synthesized by a conventional solid-liquid state reaction method. As precursors, titanium isopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), pure ethyl alcohol ( $\text{C}_2\text{H}_6\text{O}$ ), and polyvinylpyrrolidone polymer binder (PVP) have been used. All these precursors have been mixed on a hot plate for certain time. As a next step, the prepared slurry was calcined at  $900^\circ\text{C}$  for 8 hours under inert nitrogen gas ( $\text{N}_2$ ).

### 2.2. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy

With the help of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), the morphology and element distribution have been observed. The obtained results are presented in Figs. 3 and 4, respectively.

### 2.3. X-ray Diffraction

The X-ray diffraction (XRD) helps reveal the information about the crystal structure of the material along with molecular formula stoichiometry.

Figure 5 above reveals that the sample calcinated under  $900^\circ\text{C}$  contains almost 87% of sodium titanate with molecular formula  $\text{Na}_8\text{Ti}_5\text{O}_{14}$ . The theoretical capacity of this sample, if we assume a single electron transfer, is 41 mAh/g, and if we assume three electron transfers (three sodium atoms), as in the case of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , then the theoretical capacity is 124 mAh/g.

### 2.4. Electrochemical Analysis

The electrochemical testing part was made with the help of a versatile multichannel potentiostat. For this part of testing, sodium titanate with formula  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  was chosen. The cyclic voltammetry (Fig. 6) along with galvanostatic cycling with potential limitation (Figs. 7

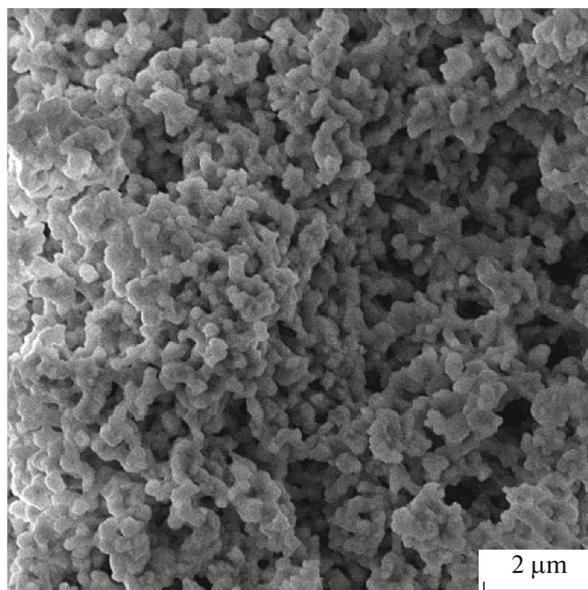


Fig. 3. SEM image of sodium titanate, under magnification 20k.

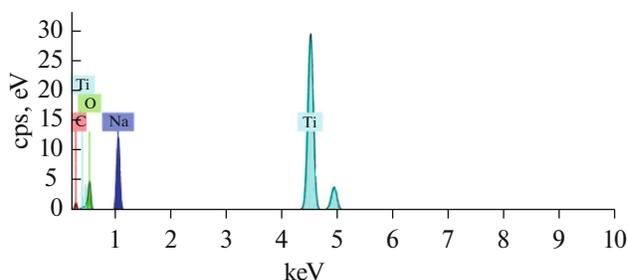


Fig. 4. EDS analysis of sodium titanate mainly confirms the presence of Na, Ti, O elements in the sample.

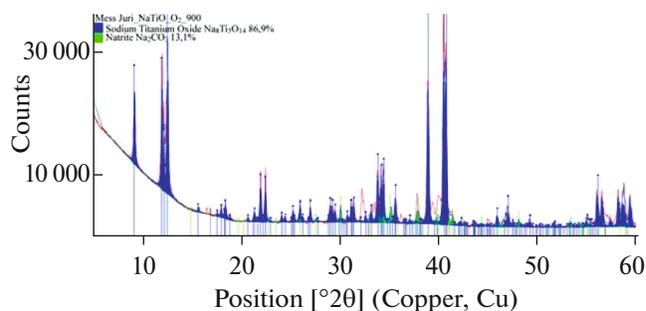
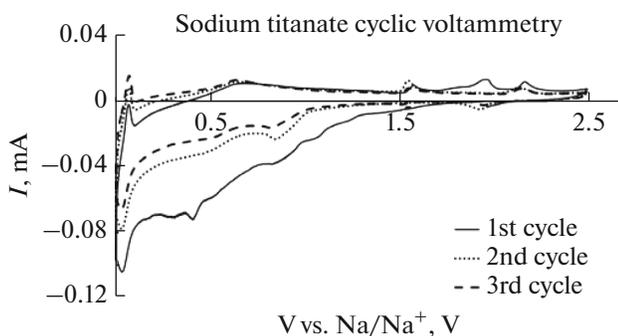


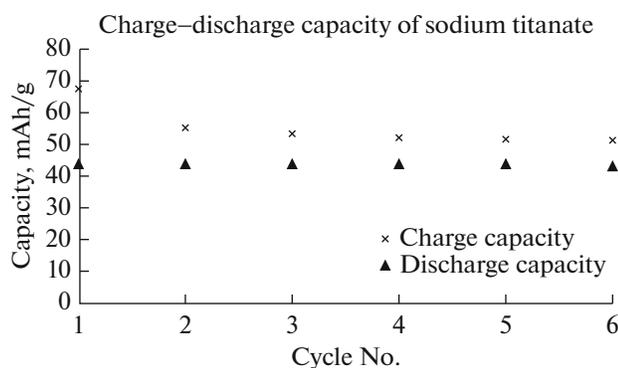
Fig. 5. XRD pattern of sodium titanate sample shows  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  phase that occupies almost 87% of the sample.

and 8) were employed to investigate electrochemical properties of the synthesized material.

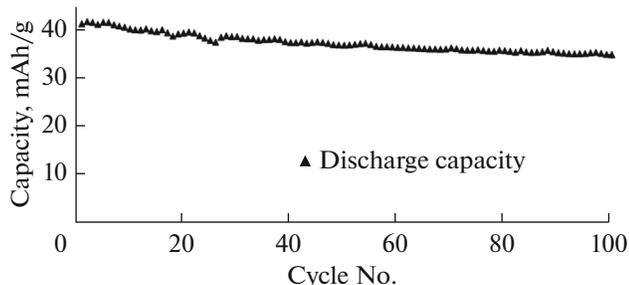
The charge–discharge capacity test results are presented in Figs. 7 and 8 below. The rate of charge and discharge was fixed to values of 0.2 C.



**Fig. 6.** Cyclic voltammetry curve of  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  sample. The related oxidation–reduction peaks, located at  $\sim 2$  V and 2.2 V, represent reversible intercalation of sodium atoms into host structure.



**Fig. 7.** First six charge–discharge cycles of capacity test.



**Fig. 8.** Discharge capacity of sodium titanate through one hundred cycles.

### 3. CONCLUSIONS

The paper deals with the preparation of sodium titanate material as negative electrode for SIBs. The pure phase of sodium titanate was synthesized (molecular formula  $\text{Na}_8\text{Ti}_5\text{O}_{14}$ ). The obtained material was subject to several analyses. Cyclic voltammetry exhibited reversible intercalation of sodium atoms, at a potential around 2 V vs.  $\text{Na}/\text{Na}^+$ . This potential is higher than the working potential of lithium titanate, that is around 1.5 V vs.  $\text{Li}/\text{Li}^+$ . The initial charge–dis-

charge cycling showed irreversible capacity and low charge efficiency in each cycle that takes approximately 12%. This may be caused by instability and decomposition of a solid electrolyte interface layer on the electrode/electrolyte interface. The overall stability within one hundred charge–discharge cycles proves and confirms the stability of metal titanate–oxide compounds and promises long durability of SIBs. Despite all disadvantages described in this article, sodium titanate is worth another research, where its main goal will be finding the proper sodium titanate stoichiometry and formula for SIBs.

### ACKNOWLEDGMENTS

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