

# NEGATIVE ELECTRODE FOR SODIUM-ION BATTERIES

**Antonín Šimek**

Master Degree Programme (1), FEEC BUT

E-mail: xsimek31@vutbr.cz

Supervised by: Jiří Libich

E-mail: libich@feec.vutbr.cz

**Abstract:** This thesis is mainly focused on research of electrode materials for negative electrodes of sodium-ion batteries, which do not use lithium for their function. It is mainly focused on the synthesis and characteristics of sodium metatitanate, which is used as active material in negative electrode mass.

**Keywords:** negative electrode, sodium titanate, theoretical capacity, energy storage, sodium-ion battery, renewable energy

## 1 INTRODUCTION

Today, battery research is a very popular topic, as they are used in almost every area of human activity. Lithium-ion batteries are used for most of this applications today, due to their large capacity and proven functionality. However, their problem is the limited amount of lithium in the earth's crust and high cost of lithium as a material. Therefore, alternatives to batteries that do not use lithium are being sought. Promising candidates are sodium-ion batteries, which could replace lithium-ion batteries in some areas. They use sodium for their function, which is abundant in the earth's crust and its price is not nearly as high as in the case of lithium.

The purpose of this work is synthesis of suitable sodium titanate, preparation of negative electrodes and their characterization in order to find a potential successor of some lithium batteries.

## 2 SODIUM-ION BATTERIES

Sodium-ion batteries were developed in parallel with lithium-ion batteries in the 1970s and 1980s, but their research was almost interrupted due to their lower capacity and more complex technological processes. In the current research, we come out from proven electrode materials, which work reliably in the case of lithium-ion batteries. However, when implementing sodium in these electrode materials, we are getting relatively different results because sodium ions are much larger than lithium ions and the resulting capacity is much smaller. However, the operating principle of sodium-ion batteries together with their basic parts is very similar to that of lithium-ion batteries. [1]

### 2.1 PROPERTIES OF SODIUM

The main disadvantages of sodium are larger dimensions and greater weight compared to lithium. The relative atomic weight of sodium is approximately  $22.99 \text{ g}\cdot\text{mol}^{-1}$ , for lithium it is only  $6.94 \text{ g}\cdot\text{mol}^{-1}$ . The potential of sodium is  $0.33 \text{ E}^\circ\cdot\text{V}^{-1}$  lower than that of lithium. Due to the greater weight, the theoretical capacity of sodium is significantly lower compared to lithium. The theoretical capacity of lithium is  $3829 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ , for sodium it is only  $1165 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ . The ionic radius of sodium is  $102 \text{ pm}$ , for lithium it is  $76 \text{ pm}$ . For this reasons, it is very difficult to find a suitable crystalline material that would accept sodium ions and at the same time show sufficient capacity and stability during cycling. [2, 3]

### 3 SYNTHESIS OF SODIUM TITANATES

The synthesis of sodium titanates was carried out by the sol-gel method, i.e. by converting the colloidal suspension into a high-purity gel, from which an oxide material in the form of a powder is formed during high-temperature sintering. The basic precursors for the synthesis of sodium titanate were: absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), Ti(IV)-ISOPropoxide ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).

The preparation procedure was as follows:

1. Using a pipette, dispense 30 ml of ethanol into a conical flask (according to Erlenmeyer).
2. Place the flask on a hot-plate, set the temperature to 90 °C and the stirring speed in the range of 120-250 rpm. Then wait for 15 minutes for ethanol to warm up.
3. Using a pipette, add 3.3 ml of Ti-ISOPropoxide to the flask and wait another 15 minutes.
4. Weigh 1,98 g of sodium carbonate and add to the flask. Wait 60 minutes for the individual substances to react.
5. Pour the resulting substance into an sintering dish and place it in to a vacuum oven.
6. Set the following parameters on the oven: temperature 800 °C, time 5 hours (300 minutes), temperature rise 3 °C.min<sup>-1</sup>, air atmosphere.

#### 3.1 SYNTHESIS OF INDIVIDUAL SAMPLES OF SODIUM TITANATES

During the synthesis, a total of 12 samples were prepared. The preparation of each sample was based on the above procedure. Different ratios of basic substances were chosen for prepared samples in order to achieve the highest possible percentage of  $\text{Na}_2\text{Ti}_3\text{O}_7$  phase in the final material, and to determine the amount of colloidal suspension, which can be reliably sintered in the laboratory furnace with sufficient purity. The prepared titanate should be a snow-white powder. Based on this information, it was therefore possible to determine whether the sample did not contain a large amount of carbon and achieved the required purity. Table 1 summarizes all the samples prepared and the amounts of starting materials used in their synthesis.

Identification	Absolute ethanol [ml]	Ti-ISO Prop. [ml]	$\text{Na}_2\text{CO}_3$ [g]	Sintering dishes [pcs]	Colour of the sample
1a, b, c, d	90	9,9	5,94	3	×
2a	30	3,3	1,98	1	Pure white
3a	30	9,9	5,94	1	Light gray
4a	30	9,9	1,98	1	Pure white
5a	60	19,8	3,96	2	Black
6a, 7a, 8a	30	9,9	1,98	1	Dark grey
9a	30	9,9	1,98	1	Pure white

**Table 1:** Summary of prepared samples and the amount of starting materials.

### 4 CHARACTERIZATION OF PREPARED SAMPLES

First, X-ray Powder Diffraction (XRD) was performed on Samples 1c, 2a, 3a and 4a. The reason for selecting these samples was their pure white colour and the assumption of a high content of sodium titanates without other impurities. Sample 4a was the best from this analysis. This sample consists of 51,1 mol. %  $\text{Na}_2\text{Ti}_3\text{O}_7$  (sodium metatitanate) and of 46.6 mol. %  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  compound. Sample 4a was therefore used for further analysis.

For further characterization, it was necessary to obtain a sufficient amount of sodium titanate. The same method of preparation sample 4a was repeated four times, thus obtaining a sample designated 9a in a total amount of 1.38 g. Scanning Electron Microscopy (SEM) as well as SEM elemental analysis were used. The result of this analysis was the following composition: 60.61 at. % of oxygen (O), 12.43 at. % of sodium (Na), 19.59 at. % of titanium (Ti) and 7.37 at. % of carbon (C).

## 5 PREPARATION OF ELECTRODES

A total amount of 0.5 g of electrode mass was prepared, where 10 wt. % was binder PVDF (polyvinylidene fluoride), 20 wt. % was conductive additive super C65 and the remaining 70 wt. % was sodium titanate (sample 9a). After preparation of the electrode mass, an 80  $\mu\text{m}$  thick layer was applied to the polished side of a 15  $\mu\text{m}$  thick copper foil. Then it was placed in a dryer at 60  $^{\circ}\text{C}$  for about 3 days.

Subsequently, the electrodes themselves were punched with a 16 mm diameter punch, which were then pressed at a pressure of approximately 25 kN for 5 seconds. The pressing process was followed by re-drying of the electrodes, but this time in a vacuum dryer at 50  $^{\circ}\text{C}$  and a pressure of 0.9 bar for about 2 days.

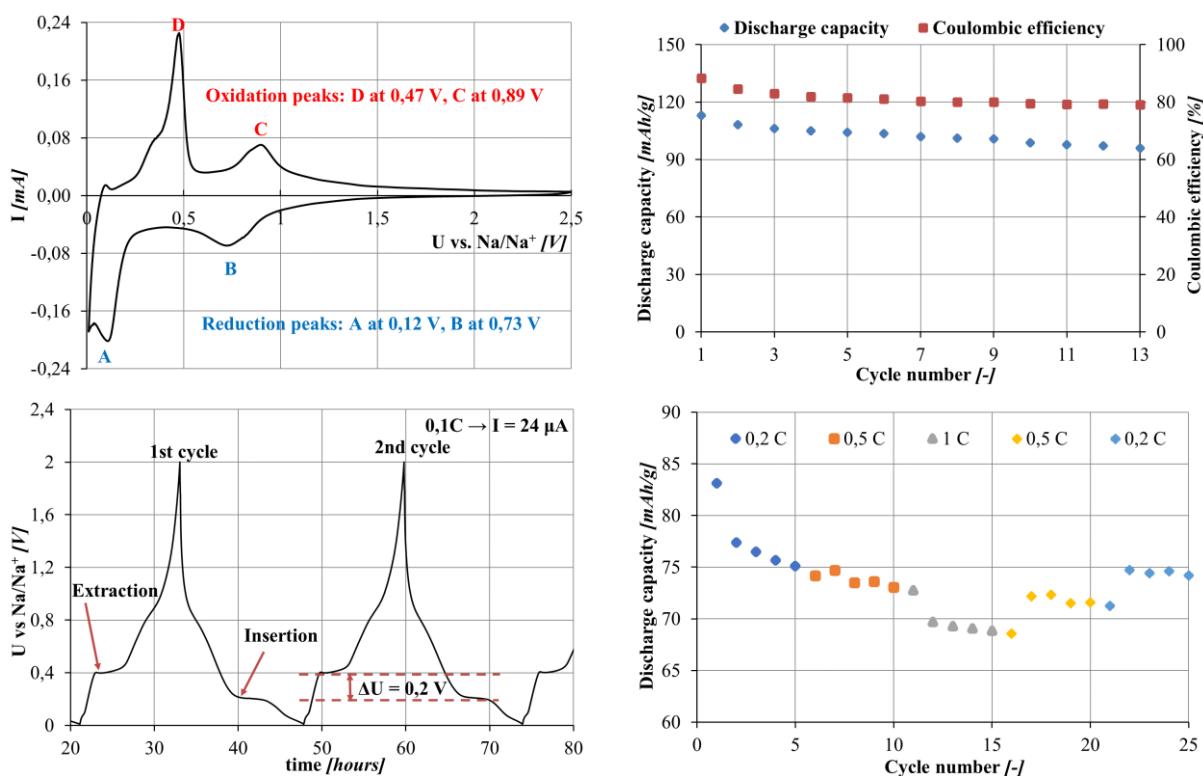
After drying, the electrodes were assembled into electrochemical measuring cells. A sodium wheel with a diameter of 16 mm and a thickness of approximately 1 mm was first placed in the cells. After that the porous separator with a diameter of 18 mm was added. This was followed by the addition of 170  $\mu\text{l}$  of liquid electrolyte type EC/DEC (cell no. 3 and no. 4) and type EC/PC (cell no. 2). Finally, the prepared electrode was added. The assembly took place in a glove box in the presence of an argon protective atmosphere.

## 6 RESULTS OF MEASUREMENTS

The measurement was performed on a multi-channel Bio-Logic potentiostat. First, an open circuit voltage (OCV) measurement was performed for 24 hours. This voltage stabilized at values in the range of 2.51 to 2.89 V for individual cells. Subsequently, Cyclic Voltammetry (CV) was performed. The plot of CV is shown in Figure 1a. Peaks A and B lying below the x-axis are located in the reduction region, where the electrode mass is charged, i.e. sodium cations are intercalated into the structure. Peaks C and D lying above the x-axis are located in the oxidation region, where the electrode mass is discharged, i.e. sodium ions are deintercalated from the structure. The measurement was compared with the measurement listed in the article [3], which we consider to be the reference. When comparing these dependences, peaks were found that lie at approximately the same potential as in the case of our measurement. Peaks A and D represents the reduction and oxidation of the  $\text{Na}_2\text{Ti}_3\text{O}_7$  phase. The remaining two peaks B and C then represents the reduction and oxidation of the  $\text{Na}_8\text{Ti}_5\text{O}_{14}$  phase.

The second measurement procedure was Galvanostatic Cycling with Potential Limitation (GCPL), which was based on CV measurements. From the theoretical capacities obtained during the CV measurement (approximately 90  $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ ), the hourly current was subsequently calculated as 1C (approximately 0.21  $\text{mA}\cdot\text{h}$ ). The electrode discharge was chosen to be 0.1C (current approximately 0.21  $\mu\text{A}$ ) to avoid unnecessary electrode overloading. This measurement showed a decrease in discharge capacity during cycling, which corresponds to be approximately 1.2 % for each cycle. The results of this measurement are shown in Figure 1b. Furthermore, horizontal sections in GCPL were measured, whose potential difference is approximately 0.2 V and which are proof of a two-phase mechanism according to the equation:  $\text{Na}_2\text{Ti}_3\text{O}_7 + 2\text{Na}^+ + 2e \rightleftharpoons \text{Na}_4\text{Ti}_3\text{O}_7$ . The GCPL results for the first two cycles are shown in Figure 1c.

The last measuring procedure was the measurement of Rate Capability (RC). In this measurement, a decrease in the discharge capacity was observed with increasing load due to the slow kinetics of the ion transition. However, the discharge capacity increases again with decreasing load, which is evidence of reversible electrochemical processes. The results of this measurement are shown in Figure 1d.



**Figure 1:** The results of measurement: (a) Cyclic voltammetry, (b) and (c) Galvanostatic Cycling with Potential Limitation, (d) Rate Capability.

## 7 CONCLUSION

The purpose of the work was to synthesize a suitable sodium titanate, to create negative electrodes and to perform their basic electrochemical characterization. The prepared electrodes showed good reversible capacity, but with a significant decrease in capacity during cycling. Nevertheless, this material is a promising candidate for the future development of sodium-ion batteries. The overlap of this work is to identify and eliminate the cause of the decrease in capacity during cycling, prepare phase-pure sodium titanate and ensure the simplest and most efficient synthesis, which could eliminate the shortcomings of existing samples..

## REFERENCES

- [1] Chem Soc Rev. ROYAL SOCIETY OF CHEMISTRY [online]. 2017, 46(12), 3485-3856 [cit. 2018-12-14]. ISSN 0306-0012. Available from: <https://pubs.rsc.org/is/content/articlepdf/2017/cs/c6cs00776g>
- [2] ŠÁTEK, Dominik. *Negative electrodes for sodium-ion batteries*. Brno, 2019. Bachelor thesis. Brno University of Technology, Faculty of Electrical Engineering and Communication. Department of Electrotechnology. Thesis supervisor Ing. Josef Máca, Ph.D.
- [3] KULOVA, T. L., Y. O. KUDRYASHOVA, A. A. KUZ'MINA, A. M. SKUNDIN, I. A. STENINA, A. A. CHEKANNIKOV, A. B. YAROSLAVTSEV a J. LIBICH. Study of degradation of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>-based electrode during cycling. *Journal of Solid State Electrochemistry* [online]. 2019, 23(2), 455-463 [cit. 2020-06-04]. DOI: 10.1007/s10008-018-4154-1. ISSN 1432-8488. Available from: <http://link.springer.com/10.1007/s10008-018-4154-1>