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# FACULTY OF ELECTRICAL ENGINEERING AND

### COMMUNICATION

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# DEPARTMENT OF ELECTRICAL AND ELECTRONIC TECHNOLOGY

ÚSTAV ELEKTROTECHNOLOGIE

# PREPARATION AND CHARACTERISATION OF CERAMIC ELECTROACTIVE MATERIALS FOR NA-ION BATTERIES

PŘIPRAVA A CHARAKTERIZACE KERAMICKÝCH AKTIVNÍCH MATERIÁLŮ PRO SODNO-IONTOVÉ AKUMULÁTORY

### MASTER'S THESIS

DIPLOMOVÁ PRÁCE

AUTHOR AUTOR PRÁCE Bc. Martin Vaněk

SUPERVISOR

VEDOUCÍ PRÁCE

Ing. Ondřej Čech

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# Diplomová práce

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Ústav elektrotechnologie

*Student:* Bc. Martin Vaněk *Ročník:* 2

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#### NÁZEV TÉMATU:

# Připrava a charakterizace keramických aktivních materiálů pro sodno-iontové akumulátory

#### POKYNY PRO VYPRACOVÁNÍ:

Zpracujte literární rešerši v oblasti keramických materiálů pro sodno-iontové akumulátory. Na základě této rešerše po dohodě s vedoucím práce vyberte materiály, které budete připravovat. Syntetizované materiály podrobte elektrochemické charakterizaci pomocí galvanostatického cyklování, cyklické voltametrie. Proveďte strukturní charakterizaci pomocí SEM a XRD. Získané výsledky vyhodnoťte.

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doc. Ing. Petr Bača, Ph.D., předseda oborové rady

#### UPOZORNĚNÍ:

Fakulta elektrotechniky a komunikačních technologií, Vysoké učení technické v Brně / Technická 3058/10 / 616 00 / Brno

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Faculty of Electrical Engineering and Communication

Department of Electrical and Electronic Technology

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#### TITLE OF THESIS:

# Preparation and characterisation of ceramic electroactive materials for Na-ion batteries

#### **INSTRUCTION:**

Based on the overview of Li-ion principles, sumarize a literature review in the field of ceramic materials for sodium-ion cells. Choose the most promising materials for Na-ion insertion, synthesize them and perform electrochemical and structural characterization of as prepared samples. Use cyclic voltametry and galvanostatic cycling for electrochemical and SEM and XRD for structural characterisation.

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doc. Ing. Petr Bača, Ph.D. Subject Council chairman

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#### Abstract

The major aim of this work is characterisation of the titanate samples as materials for sodium-ion (Na-ion) batteries. Some of them were synthesized within this thesis. The characterisation is focused on electrochemical properties, composition and morphology of used materials.

The firs part deals with lithium-ion (Li-ion) batteries. They were chosen because they are well described in science articles and the basic operation principle explained in this chapter is also applicable to the Na-ion batteries. Materials used for cathodes, anodes and electrolytes follows the short section about parameters and construction of the Li-ion batteries.

The next chapter is focused on the Sodium-ion batteries. There is comparison of sodium and lithium at the beginning of this chapter, followed by materials used for electrodes and electrolyte (with emphasis on anode materials).

The third part describes analysis methods used for characterisation of electrode materials. It includes electrochemical characterisation (cyclic voltammetry and galvanostatic cycling with potential limitation), morphology (scanning electron microscopy) and composition (X-ray diffraction spectroscopy).

Last two chapters include synthesis and characterisation of sodium titanate and characterisation of two samples of  $TiO_2$ . Results of this work are summarized in the conclusion.

#### **Keywords**

Anode, battery, capacity, galvanostatic cycling, intercalation, ion, lithium, SEM, sodium, titanate, voltammetry, XRD

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#### INTRODUCTION

The number of electronic devices is increasing every day. This phenomenon is linked with need of electrical sources to power them. The most of portable electronic devices contains electrochemical energy source, the small minority contains alternative power sources like photovoltaic cells or micro energy harvesting systems.

The vast majority of portable devices like mobile phones or notebooks are powered by the Lithium-ion (Li-ion) batteries. First primary Li-ion batteries were invented in the mid-sixties of 20. century. They had high capacity and low self discharge. First commercial device with Li-ion rechargeable battery appeared in January 1991. It was mobile phone "Handyphone HP-211" made by SONY. A year later, in September 1992, SONY introduced first video camera with Li-ion battery. 193 million Li-ion batteries were manufactured in 1997 (98 % of this amount was made in Japan).

The research of sodium-ion (Na-ion) and lithium-ion batteries was done simultaneously at the beginning. Later on the Li-ion batteries had better properties, became usable for commercial purposes and focus of researchers moved mostly on this type of batteries. The Li-ion batteries are well described in the literature and their principle is identical with Na-ion batteries. It is the reason for choosing them as a theoretical background of this work.

Li-ion batteries have high typical nominal voltage 3,6 V (concrete value depends on electrolyte and electrode materials) in comparison with 1.2 V of NiCd and NiMH batteries. [18] Energy density of Li-ion batteries is very high and can reach 190 Wh/kg [19] and according to some sources it can be even more than 200 Wh/kg . Another advantage is low self-discharge that is typically few per cent per month, but it strongly depends on storage temperature. Self-discharge of NiMH batteries varies approximately from 20 % to 25 % and for NiCd batteries it is from 15 % to 20% [6]. Good-quality Li-ion batteries can usually be recharged more than thousand times, special ones can be recharged even 12000 times [19]. They don't contain toxic metals like lead or cadmium and usually withstand temperatures from -20 °C up to 60 °C [19]. Li-ion batteries were more expensive alternative to the other types of batteries in past, but their price is decreasing. Their approximate price is now 0.4 \$/Wh (depends on concrete type) [19].

Li-ion batteries have also some disadvantages. They have limited charge and discharge current and nominal voltage is decreasing during discharge. Voltage drop can be problematic for some applications, but on the other hand it is good indicator for monitoring the level of discharge. Li-ion batteries are sensitive to overcharging and overdischarging. [18] Both these states can cause irreversible changes making the battery useless. Overcharging is more dangerous because it can lead to the destruction of the battery.

During last years, sodium-ion batteries returned back to the focus of researchers. The reasons could be the limited reserves of lithium and increasing demand for large-scale electricity storage systems where the energy density is not crucial.

#### **1 LITHIUM-ION BATTERIES**

Lithium-ion batteries is the term for wide range of electrochemical sources that use lithium ions as charge carriers. There are many types of Li-ion batteries with different parameters like electrodes materials, electrolyte and construction. This parameters influence nominal voltage, number of charging cycles and temperature characteristics to name but a few. Following sections describe operating principle of Li-ion batteries, their construction and materials used for electrodes and electrolyte.

#### **1.1** Operating Principles of Li-ion Batteries

Operating principle of Li-ion batteries will be described on the common type with  $LiCoO_2$  cathode and graphite anode. Current collectors are usually made of aluminium (cathode) and copper (anode). Charging and discharging process is schematically shown in figure 1.1. Lithium ions are moving from graphite anode to  $LiCoO_2$  cathode during discharge. This process causes electrons in external circuit to flow from anode to cathode. The process of discharge is reverse - electrons from outer source are moving towards anode and lithium ions move from cathode to anode. Electrolyte is conductive for ions but non-conductive for electrons.



Fig. 1.1: Charge and discharge process in Li-ion battery [19]

There are chemical changes on cathode and anode during charging and discharging. This process is described by equation 1.2 (cathode reaction) and 1.3 (anode reaction). Both these reactions take place simultaneously and are linked with electron exchange through the outer circuit. It shows the process of charging from the left side of the equations to the right. The opposite direction describes discharging. During discharging, lithium ions from graphite anode move to  $\text{LiCoO}_2$  cathode. Electrons from anode oxidation reaction flow through outer circuit to cathode where they cause reduction of lithium ions. [20]

$$LiCoO_2 \quad \leftrightarrows \quad Li_{1-x}CoO_2 + xLi^+ + xe^-$$
 (1.2)

$$C + xLi^+ + xe^- \quad \leftrightarrows \quad CLi_x \tag{1.3}$$

Process taking place in graphite anode and lithium metal oxide cathode is called intercalation. It is reversible inclusion of one particle (atom/ion) between two other particles. Lithium forms a solid solution with the intercalation host. In the case of graphite anode, it is inclusion of lithium ion between carbon atoms. Graphite consists of layers made up from carbon atoms connected by covalent bond into hexagons (so called honeycomb lattice). These layers are bond together by the week van der Walls forces. This structure enables inclusion of lithium ions. Materials for cathodes must be intercalation compounds too. They must accommodate lithium ions without damage and excessive structural changes. Lithium must be part of it during manufacturing because Li-ion batteries are assembled as discharged.

One electron transferred through the external circuit equals one lithium ion moved from cathode to anode (during discharge). Open circuit voltage is determined by the potential of lithium in positive and negative electrode. The voltage of the Li-ion cell can be calculated from equation 1.4,

$$V = -\frac{\mu_{Li}^{int} - \mu_{Li}^{graph}}{F} \tag{1.4}$$

where  $\mu_{Li}^{int}$  and  $\mu_{Li}^{graph}$  are potentials of lithium in cathode and anode respectively, F is Faraday constant (approximately 96485 C·mol<sup>-1</sup>). Higher difference in potential of electrodes results in higher voltage of Li-ion battery. When the battery is fully charged, lithium ions are accommodated by the graphite anode (state of high potential  $\mu_{Li}^{graph}$ ). Lithium ions are moving to the cathode characterised by the lower potential  $\mu_{Li}^{int}$ . Due to this process, work in the external circuit can be done. Chemical potential of electrodes is changing during charging and discharging. Potential of positive intercalation electrode is therefore measured against lithium metal. Lithium as intercalation compound mostly exists as lithium ion along with charge-compensating electrons. These electrons are located in the d orbital of the transition metal forming the cathode. Potential of lithium intercalated in cathode can be thus written as

$$\mu_{Li}^{int} = \mu_{Li^+}^{int} + \mu_{e^-}^{int} \tag{1.5}$$

where  $\mu_{Li^+}^{int}$  stands for chemical potential of lithium ions and  $\mu_{e^-}^{int}$  is chemical potential of electrons. Energy of electrons inserting into intercalation host (electrode) equals the Fermi level. Electrode potential of graphite electrode is approximately from 10 to 800 mV versus lithium. Potential of cathode must be higher to obtain the same voltage of the cell in comparison with lithium metal anode. [5]

The aim is to get low Fermi level. It is determined by the top of the valence band of the intercalation compound. Electron configuration of oxygen is  $1s^2 2s^2 2p^4$ 

and electron configuration of sulphur is [Ne]  $3s^2 3p^4$ . This means that valence band of oxides lies significantly below the the top of valence band of the corresponding sulphides. Fermi level in oxides can be more than 2 eV lower and potential versus Li/Li<sup>+</sup> can be from 4 to 5 V. Fermi level of transition metal oxides is given by the position of the cation d levels. Transition metals like chromium, iron, manganese, cobalt and nickel have d levels close to the top of the oxygen valence band. [5]

Lithium has high redox potential causing majority of salt or solvents becoming thermodynamically unstable. Stability of lithium in Li-ion batteries is given by so called solid electrolyte interface (SEI). One or more electrolyte components react with lithium and products of such reaction form the thin layer on the electrode surface. This film is nonconductive for electron and conductive for ions. The term solid electrolyte interface is usually used for graphite or metallic lithium anodes only. At the beginning, non-aqueous electrolytes based on propylene carbonate (PC) were used. Unfortunately, the decomposition product of PC was unable to protect graphite layer structure. Many years later, electrolyte based on ethylene carbonate (EC) was used. The interface formed by EC enabled reversible intercalation of lithium ions. This was great advance in technology of Li-ion batteries.

Electrolytes based on organic carbonates with cyclic or acyclic structure are usually used in Li-ion batteries because they can form stable interface on transition metal oxides. Cyclic carbonates are for example ethylene carbonate (EC) and propylene carbonate (PC). Acyclic carbonates include dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC) etc. Figure 1.6 shows one cyclic (EC) and one acyclic carbonate (DMC).[30]



Fig. 1.6: Chemical formula of ethylen carbonate (left) and dimethyl carbonate (right)

Oxidative and reductive decomposition processes were investigated, but with more emphasis on the reductive process on graphite anode. Large solvent molecules cointercalating to graphite along with lithium ions usually causes exfoliation o graphite layers that are held together by week van der Waals forces. Distance between hte graphite layers decreases from 1.59 nm down to approximately 0.35 nm due to SEI formation. Intercalation and deintercalation of Li<sup>+</sup> then causes volume change of less than 10 %. This cyclic volume change during charging and discharging is so-called "breathing effect". [30]

Intercalation is not the only electrode reaction mechanism in lithium-ion batteries. Possible reaction mechanisms are shown in figure 1.7.



Fig. 1.7: Schematic illustration of reaction mechanisms of electrode materials [16]

#### **1.2** Parameters and Construction of Li-ion Batteries

Apart from nominal voltage, volumetric and gravimetric energy density are important parameters of batteries. This quantities determine the amount of energy that can be stored per unit volume or weight. Some applications prefer high gravimetric energy density (e.g. electric vehicles) while other appreciate high volumetric energy density (e.g. medical implants). Volumetric (gravimetric) density is given by equation 1.8,

$$E = V_e \cdot Q \tag{1.8}$$

where E is volumetric (gravimetric) energy density,  $V_e$  is electrode potential and Q is charge that can be stored by intercalation compound per unit volume (mass). Volumetric (gravimetric) energy density is usually given in Wh/l (Wh/kg). Electrode potential has been mentioned in the previous section. Charge that can be stored is equivalent to the amount of lithium that can by accommodated by the electrode.

Charge and discharge current of Li-ion cells is limited by the rate of lithium ion intercalation and deintercalation. Charge neutrality causes that one electron in outer circuit equals to exchange of one lithium ion in the cell. Electrodes must be capable of cyclic intercalation and deintercalation and must form stable interface with electrolyte. [5]

Li-ion batteries are manufactured in various sizes and shapes. 1.9 shows cylindrical and pouch types. As can be seen they consist of case with positive and negative terminal. The case encloses electrodes, separator and electrolyte and provide mechanical protection. Cathode and anode are separated by special porous separator. Typical thickness of electrodes varies from 60 to 100  $\mu$ m [21]. Electrodes layers are from both sides of current collector foils (Aluminium foil for cathode and copper foil for anode). The material and structure of separator must enable ions going through it from one electrode to another. Its thickness is usually between 15 and 25  $\mu$ m [21]. Separator also serves as non conductive barrier to avoid short circuit between electrodes. This function is important because short circuit in the Li-ion cell can cause its ignition. Li-ion batteries can also include monitoring circuitry to prevent overcharging and overdischarging.



Fig. 1.9: Construction of cylindrical (left) and pouch (right) Li-ion cell [19]

#### **1.3** Cathode materials

First commercially successful Li-ion batteries used lithium cobaltate (LiCoO<sub>2</sub>) cathode together with carbon anode an non-aqueous electrolyte. Cathodes are the key elements limiting the performance of Li-ion batteries and they are also the most expensive part of it. Research of cathodes is mostly focused on the transition metal oxide compounds enabling large mobility of the lithium ions. Important factor of the material is its crystal structure. There are three basic structures used for this purpose. First one was layered structure of LiCoO<sub>2</sub> (since 1980), second one was spinel structure of LiMn<sub>2</sub>O<sub>4</sub> (since 1986) and the last one was olivine structure of LiMPO<sub>4</sub> (since 1997) where M stands for Fe, Mn etc. All mentioned materials achieve theoretical specific capacity higher than 140 mAhg<sup>-1</sup> at potential higher than 3.4 V versus Li/Li<sup>+</sup>. Table 1.10 summarizes specific capacity and average potential of the basic cathode compounds. Practical specific capacity of mentioned compounds varies from 120 to 200 mAhg<sup>-1</sup>. The layered compounds have the highest theoretical specific capacity and spinel compounds has the lowest. On the other hand, spinel compound LiMn<sub>3/2</sub>Ni<sub>1/2</sub>O<sub>4</sub> has the highest average potential 4.7 V. [13]

The crystal structure determines the possibilities of movement of the lithium ions in the cathode. Layered structure enables movement of ions in two dimensions (2D), spinel structure in three dimensions (3D) and olivine structure in one dimension (1D). Crystal structures of all three classes are shown in figure 1.11. Properties, advantages and disadvantages of basic types of cathode compounds will be described in the following part of this section. [13]

Framework	Compound	Specific capacity *	Average potential
Framework	Compound	$(mAhg^{-1})$	(V vs. $Li/Li+$ )
Lavorod	$LiCoO_2$	272(140)	4.2
Layered	$\mathrm{LiNi}_{1/3}\mathrm{Mn}_{1/3}\mathrm{Co}_{1/3}\mathrm{O}_2$	272 (200)	4.0
Spinol	$LiMn_2O_4$	148 (120)	4.1
Spiller	$\rm LiMn_{3/2}Ni_{1/2}O_4$	148 (120)	4.7
Olivino	$\rm LiFePO_4$	170(160)	3.45
Onvine	${\rm LiFe}_{1/2}{\rm Mn}_{1/2}{\rm PO}_4$	170 (160)	3.4/4.1

**Tab. 1.10:** Properties of the three classes of insertion compounds [13]

\* values in parenthesis indicate the practical specific capacity of electrode



Dimensionality of the Li<sup>+</sup>-ions transport

Fig. 1.11: Crystal structure of layered, spinel and olivine insertion compounds [13]

#### 1.3.1 Layered Compounds

Typical layered compounds are  $LiCoO_2$  (LCO) and  $LiNiO_2$  (LNO). Oxygen ions have cubic arrangement, transition metals together with lithium ions form octahedral structure. Structure of LCO is shown in figure 1.11.

Cobalt is trivalent in LCO. During charging and discharging,  $Li^+$  ions create and annihilate vacancies in the layered structure. Distribution of Lithium ions causes transitions of crystal structures. Surface modification is used to prevent metal ion dissolution in electrolyte followed by oxygen release. Materials effectively preventing cathode breakdown are for example  $ZrO_2$ ,  $Al_2O_3$  and  $TiO_2$ . [13]

 $LiNiO_2$  has the same structure as  $LiCoO_2$ . Both nickel and cobalt are present in 3+ and 4+ oxidation states. Li-ion cell with LNO cathode has nominal voltage approximately 4 V (close to LCO). However, LNO has few disadvantages. Firstly, it is difficult to synthesize LNO with all Ni<sup>3+</sup> ions that are well distributed, because mixing of Li<sup>+</sup> and

 $Ni^{3+}$  ions in lithium plane can occur. This compound is therefore better characterised by  $Li_{1-z}Ni_{1+z}O_2$  formula. Another problem is irreversible phase transition that occurs during charge/discharge cycles. Beside other difficulties, there are also safety concerns. Exothermic release of oxygen at elevated temperatures can be dangerous in the charged state. According to its properties, LNO is not suitable material for commercial Li-ion batteries. However, cathodes combining LNO and LCO exhibit good reversible capacity and excellent cycling properties. [13]

FIgure 1.12 shows charge-discharge cycle of  $\text{Li}_x \text{CoO}_2$ . Voltage varies from 3.6 V to 4.85 V and X varies from 1 to 0.05. LCO compound undergoes several phase changes during the cycle. Repeated cycles caused cathode degradation and fatigue. The layered structure  $\text{LiNi}_y \text{Mn}_y \text{Co}_{1-2y} \text{O}_2$  (NMC) was studied as possible successor of LCO. It has better stability at elevated temperature and reversible capacity 200 mAhg<sup>-1</sup> (in the cutoff range from 2.8 V to 4.6 V). Manufacturing is the main problem because of mixing between lithium and nickel ions. Such mixing is caused by the similar ionic radius of these elements. [13]



Fig. 1.12: Charge-discharge curves of  $Li_x CoO_2$  at C/24 rate [13]

#### 1.3.2 Spinel Compounds

Spinel cathode compounds are represented by  $\text{LiMn}_2\text{O}_4$  (LMO) and  $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$  (LNM). LNM is made from LMO by substituting 25 % of manganese in LMO by nickel. Manganese in LNM is in the 4+ valence. This condition avoids Jahn-Teller distortion that is possible for  $\text{Mn}^{3+}$ . Electrochemical activity is due to the redox reactions of Ni<sup>2+</sup> ions in LNM compound. [13] It is difficult to synthesize pure LMO, because there are usually impurities like NiO or  $\text{Li}_y \text{Ni}_{1-y} O$ . Partial replacement of Ni and Mn by chromium stabilizes the lattice, but it has negative impact on energy density. [13]

LMO has good structural stability during charge-discharge cycles. On the other hand, it suffers with irreversible loss of capacity especially at elevated temperature. Figure 1.13 shows discharge characteristic of a  $\text{Li}//\text{LiMn}_2\text{O}_4$  cell. LMO Cathode was synthesized at 700 °C. Specific capacity of LMO is limited to less than 120 mAhg<sup>-1</sup> around 4.1 V. [13]



Fig. 1.13: Voltage discharge profile of a  $Li//LiMn_2O_4$  cell at C/24 rate [13]

#### 1.3.3 Olivine Compounds

One of the olivine compounds is LiFePO<sub>4</sub> (LFP) crystallizing in orthorhombic system. Its theoretical specific capacity is 170 mAhg<sup>-1</sup>. Its advantages are low price and no toxicity. Nevertheless, it has low electronic conductivity and low diffusion coefficient of lithium ions. This properties can result in capacity loss during high-rate discharge. This drawbacks can be partially reduce by the way of manufacturing (using nano-size particles). Carbon coating also enhance cathode performance. [13]

#### **1.4** Anode Materials

Anode is another part of the Li-ion battery that determines its properties. It influences not only nominal voltage of the cell, but also other parameters like (dis)charge rate, number of cycles or temperature stability. Important is not only the material, but also the structure of anode. Research is focused on nanomaterials and nanocomposites, because decreasing particle size improves electrode properties. The most commonly used negative electrodes are based on graphite (carbon). Less used are anodes made from lithium titanate. This two materials will be described in the following part. Research also focuses on different materials like Si, Sn or  $SnO_2$  [12].

#### 1.4.1 Carbon Based Anodes

Carbon anodes use different modifications of this element. The most common is graphite anode. Research is also focused on graphene and graphene/graphite nanoparticles. Not only electrochemical properties, but also price and ease of manufacturing must be taken into account.

#### Graphite Anodes

Graphite anodes are the most frequently used anodes and are combined with different cathodes. One of their advantages is small volume change during intercalation and deintercalation. Despite small volume change of approximately 10 %, repeated intercalation can lead in some cases to the structural failure. The composition of anode is changing from C to  $\text{LiC}_6$  during charging process. Table 1.14 shows computed values of average polycrystalline Young's modulus and Poisson's ratio of graphite, lithium and graphite with different amount of intercalated lithium. There is apparent strong impact of lithium content in graphite.  $\text{LiC}_6$  has more than 3.5 times higher Young's module in comparison with  $\text{LiC}_{18}$ . Increase of the Young's modulus is linked with decrease of Poisson's ratio, that is the ratio of transverse (normal to the applied load) and axial strain (in the direction of the applied load). [1]

	Average Polycrystalline		
	Young's Modulus	Poisson's Ratio	
	E (Gpa)	$\mu$ (-)	
Graphite	32.47	0.32	
LiC <sub>18</sub>	28.57	0.39	
${\rm LiC_{12}}$	58.06	0.34	
${ m LiC_6}$	108.67	0.24	
Li	2.00	0.34	

Tab. 1.14: Computed values of Young's modulus and Poisson's ratio [1]

Graphite anodes are so widely used because of their low price, low operating potential (resulting in high voltage of lithium battery), high capacity, high reversibility and structural stability. Figure 1.15 shows the structure of graphite that consists of individual graphene layers bond together by weak van der Waals forces. The diffusion coefficient of lithium ions in the graphite (in direction parallel to the graphene layers) is approximately  $10^{-6}$  cm<sup>2</sup>s<sup>-1</sup> [23].



Fig. 1.15: Graphite structure with diffusion coefficient [23]

#### Graphene Nanoflakes Ink Anodes

Another type of anodes using carbon is graphene nanoflakes ink anode. Together with lithium iron phosphate cathode it has specific capacity  $165 \text{mAhg}^{-1}$ , estimated energy density of about  $190 \text{Whkg}^{-1}$  and stable operation for over 80 cycles. Using printing technologies, graphene nanoflakes ink anodes are cheap and scalable. Advantage of graphene is its high surface to mass ratio (more than  $2600 \text{ m}^2\text{g}^{-1}$ ). It has also high electrical conductivity and high mechanical strength. Graphene nanoflakes ink on copper base can reach specific capacity approximately  $1500 \text{ mAhg}^{-1}$  at a current rate of  $100 \text{ mAg}^{-1}$  over 150 cycles. [12] Grahpene nanoflakes are made from graphite. The production process is shown in figure 1.16. In the first step, graphite layers are separated by low-power ultrasonication in N-Methyl-2-Pyrrolidone. Separation of graphite layers is called exfoliation. The next step is ultracentrifugation that enables sorting of graphite flakes according to their size based on different sedimentation rate. The aim is to get nanoflakes smaller than 100 nm to obtain the optimal parameters of anode. The final graphene ink consists of single layer graphene (SLG) and few-layer graphene (FLG) flakes typically varying in size from 30 nm to 100 nm. [12]



Fig. 1.16: Graphene nanoflakes production process [12]

Anode is made by drop casting the graphene in on a polycrystalline copper support. It is done in ambient conditions at 140 °. Sample is than annealed at 400 ° under ultrahigh vacuum to remove solvents and avoid reaction with ambient atmosphere. Nanoflakes give the electrode excellent electrical properties, that are important for electron transport to the external circuit. [12]

#### 1.4.2 Lithium Titanate (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) Based Anodes

Lithium titanate (LTO) is another possibility of anode material. When discharged, its composition is  $Li_4Ti_5O_{12}$ . It has spinel crystal structure in this state. It accommodates lithium ions during battery charging and transforms to  $Li_7Ti_5O_{12}$ . Both configurations are shown in figure 1.17. This transition is connected with transformation from spinel to rock salt structure. One of the advantages of LTO is small volume change during chargedischarge cycles. The lattice parameter changes from 8.3596 to 8.3538 Å, that is less than 0.1 %. [22]



Fig. 1.17: Spinel (left) and rock salt (right) configuration of LTO [26]

Working potential of LTO is 1.55 V vs. Li/Li<sup>+</sup>. This means that Li-ion battery with lithium titanate anode has typical voltage of around 2.5 V which is approximately 1 V less in comparison with graphite anode battery. On the other hand, lower voltage means that electrolyte stays within its stability window. In consequence, formation of SEI is limited and irreversible capacity loss is reduced. Another advantage is that aluminium current collector can be used instead of copper due to the higher working potential of LTO anode. Aluminium collector means reduction of manufacturing costs. Batteries with LTO are also safety, because higher potential reduces the risk of metal lithium formation on the anode surface. [22]

Forming a lithium battery of LTO anode and LMO cathode gives us a working potential of 2.5 V. LTO very stable and can still have more than 80 % of its initial capacity after several thousand cycles. Therefore, this material is perspective for applications with high demands on cycling and lifetime. Negligible volume change during charging and

discharging also enables high charge and discharge rate without structure damage of anode. This properties are important for example for using in hybrid or electric vehicles. [22]

#### 1.4.3 Silicon Based Anodes

Anodes based on silicon are studied for its extremely large theoretical specific capacity. Practical limit of silicon anode capacity is  $3579 \text{ mAhg}^{-1}$  in the pure phase [21]. Theoretical specific capacity is  $4200 \text{ mAg}^{-1}$ , but such a large intake of lithium leads to approximately 300 % increase of volume [24]. Crystalline Si (c-Si) expand anisotropically during lithiation. Nanotructures are used to avoid cracks caused by the volume changes stress. On the other hand, lithiation and volume expansion of amorphous Si (a-Si) is isotropic. [21]

The diffusion coefficient of lithium in silicon varies from  $10^{-13}$  to 10-11 cm<sup>2</sup>s<sup>-1</sup>. Slow diffusion can cause high lithium concentration near the Si surface, causing large stress and volume changes. Research showed that fabrication methods and structure have high impact on Si anodes performance. Proper nanostructures enables good lithium transport and prevent cracking. Various composites of silicon with carbon were also studied. Despite the progress of the Si anodes research, they are still not used in commercially available batteries because of the volume changes and cracking during insertion and extraction of lithium. [21]

#### 1.4.4 Germanium based anodes

Germanium (Ge) has very good conductivity and lithium diffusivity in comparison with silicon. Insertion of lithium leads to intermediate lithiated crystalline phases until Li15Ge4 is ultimately formed. Lithium extraction results in formation of a porous amorphous phase. The whole process is isotropic and does not lead to material cracking. Thin-film experiments shown even at rates of 1000 C. The advantage of germanium over silicon is that germanium anodes can be formed of larger particles because of its properties. It is linked with reduction of SEI formation that influences irreversible capacity and impedance. Disadvantage of Ge electrodes is their high cost. [21]

#### 1.4.5 Other Anode Materials

There is wide range of materials that are (or have been) studied. Research was focused for example on transition metal (Fe, Co, Cu, Mn,...) oxides, nitrides, phosphides and hydrides [21]. Nevertheless, there is usually one or more disadvantages that make the material not suitable for the commercial use.

#### **1.5** Electrolytes

Electrolyte consists of ions dissolved in some medium (liquid or solid). Electrolytes can be water-based (for example NaCl dissolved in water) but this type of electrolytes is not suitable for Li-ion batteries. Water would dissociate due to the higher voltage of Li-ion batteries and formation of lithium metal would generate hydrogen and heat. This combination could cause explosion of the battery.

Instead of water based electrolytes, Li-ion batteries use organic solvent based electrolytes. Their composition is selected to meet required properties. They should have sufficient concentration of lithium salt and good ion conductivity, they must be compatible with all battery parts (including good wetting) and they should be temperature stable and resistant to excessive ageing. Their stability must be high enough to withstand the voltage in the battery. Electrolytes can be in liquid or solid state, but liquid state ones are preferred because of their better conductive properties.

Electrolytes are usually a mixture of a few solvents that adjust its individual properties (e.g. dielectric constant, viscosity and melting/boiling point) and a lithium salt. The dielectric constant  $\varepsilon$  determines the amount of salt that can be dissolved in solvent. Higher dielectric constant means higher amount of salt that can be dissolved. Viscosity determines ability of electrolyte to be in good contact with electrodes (good wetting of electrodes). Melting and boiling points should be chosen according to storage and operating temperature range. Electrolyte should resemble in one phase (usually liquid) within this temperature range. Electrolytes are often complex mixtures of solvents and additives that are kept secret by the manufactures. [20]

Table 1.18 lists some solvents used for lithium battery electrolytes, their melting point, boiling point and dielectric constant. Cyclic esters like propylene carbonate or ethylene carbonate have high viscosity. Therefore, these solvents are mixed with solvents like dimethyl carbonate (DMC) or diethyl carbonate (DEC), that have low viscosity. Research was also focused on other solvents that could replace alkyl carbonates. They are for example trans butylenes carbonates, chlorinated or fluorinated carbonate. These solvents are suitable for graphite electrodes and could replace EC, that has high melting point.[4]

The most of commercial lithium batteries use  $\text{LiPF}_6$  (lithium hexafluorophosphate) salt dissolved in ethylene carbonate (high dielectric constant, high viscosity) and a mixture of other low viscosity alkyl carbonates. Advantage of  $\text{LiPF}_6$  is high conductivity for lithium ions and good dissociation, but it has limited thermal stability. The biggest disadvantage is reaction with water. In contact with water, it forms hydrofluoric acid (HF) that reacts with graphite and forms a film consisting of LiF. This film is poor ionic conductor and causes increase of impedance between the electrode and electrolyte. Another studied salts are for example LiClO<sub>4</sub>, LiAsF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub> and LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>. [4]

 $LiClO_4$  (lithium perchlorate) and  $LiAsF_6$  (lithium hexafluoroarsenate) are not used commercially because of the risk of explosion and toxicity of arsenic and its compounds.  $LiBF_4$  (lithium tetrafluoroborate) has low conductivity, but according to observations it has good performance at low temperature.  $LiCF_3SO_3$  (lithium trifluoromethanesulfonate) has poor ionic conductivity and causes corrosion of aluminium collector (same problem with  $LiN(SO_2CF_3)_2$ ). [4]

Solvent name	Melting point	Boiling point	Dielectric constant	
(abbrev.)	$(^{\circ}\mathbf{C})$	(°C)	ε	
Ethylene carbonate	39-40	248	89.6 (40°C)	
(EC)	33-40	240	(40 C)	
Propylene carbonate	40	240	64.4	
(PC)	-49	240	04.4	
Dimethyl carbonate	4.6	01	2 1 9	
(DMC)	4.0	91	0.12	
Diethyl carbonate	42	196	0.80	
(DEC)	-40	120	2.02	
2-Methyl-tetrahydrofuran	137	70	6 20	
(2Me-THF $)$	-157	19	0.29	
Dimethoxy ethane	58	85	7 20	
(DME)	-99	00	1.20	
$\gamma$ -Butyrolactone	/3	204	30.1	
$(\gamma$ -BL)	-40	204	53.1	

 $\textbf{Tab. 1.18:} \ \textit{Properties of some solvents used for lithium battery electrolytes [4]}$ 

#### 2 SODIUM-ION BATTERIES

Sodium (Na) is the second lightest alkali metal after lithium (Li). It has atomic number 11 and calculated atomic radius 190 pm. To compare with, lithium has atomic radius 167 pm. Comparison of various properties of lithium and sodium is listed in table 2.1. As lithium and sodium are in many ways similar, researchers began to focus also on sodium as a possibility for new generation of rechargeable batteries.

The advantage of sodium is that it is one of the most abundant elements on Earth, while lithium is much less abundant. This could be beneficial especially for the large scale storage where the higher weight, caused by lower gravimetric energy density of sodium-ion batteries, is not so important as in lightweight portable devices. [16]

Potential of sodium is -2.71 V vs. standard hydrogen electrode (SHE) causing voltage of sodium-ion battery to be approximately 0.3 V lower than equivalent lithium-ion battery. Another disadvantage is higher atomic radius which must be taken into account during design of electrodes. Atomic weight of sodium is more than three times higher than atomic weight of lithium. As consequence of more than three times higher atomic weight, sodium has more than three time lower theoretical capacity than lithium (1165 mAhg<sup>-1</sup> vs.  $3829 \text{ mAhg}^{-1}$ ) [10].

	Lithium	Sodium
Atomic number	3	11
Electron configuration	[He] $2s^1$	[Ne] $3s^1$
Atomic radius	167 pm	190 pm
Electronegativity	0.98	0.93
Valence	1	1
Melting point	180.54 °C	97.72 °C
Boiling point	1342 °C	883 °C
Auto-ignition point	179 °C	115 °C
Density	$0.535 \text{ g} \cdot \text{cm}^{-3}$	$0.968 \text{ g} \cdot \text{cm}^{-3}$
Atomic weight	$6.941 \mathrm{~g/mol}$	22.98977  g/mol
Electrical conductivity	$1.1 \cdot 10^7 \ {\rm S} \cdot {\rm m}^{-1}$	$2.1 \cdot 10^7 \text{ S} \cdot \text{m}^{-1}$
Potential vs. SHE	-3.04 V [10]	-2.71 V [10]
Crystal structure	body centered cubic	body centered cubic
Lattice constant	351 pm	429.06 pm

Tab. 2.1: Chosen properties of lithium and sodium

Data acquired from http://periodictable.com/

#### 2.1 Cathode Materials

Research of cathode materials for sodium-ion batteries partially derived from the lithium-ion batteries. It was confirmed that not all of the materials suitable for Li-ion batteries are also suitable for Na-ion batteries. It is given by the partially different properties of those element. Oxide compounds, probably the most studied type of cathode compounds. are described in this section.

#### 2.1.1 Oxide compounds

Layered Na<sub>x</sub>MO<sub>2</sub> (M is transition metal) compounds are studied as one of the potential materials for Na-ion cathodes. They can be found in different crystal structures. They can possess On structure (notation according Delmas et. al.) where Na is octahedrally coordinated by oxygen (n stands for the repeat period of the transition metal stacking). The other structure is Pn where Na atoms occupy trigonal prismatic sites. Gliding of MO<sub>2</sub> sheets causes phase transition between Pn and On. Such transitions are possible also at room temperature (transition between Pm and On, where m  $\neq$ n, is possible only at high temperature because it is connected with break of M-O bonds). [16]

One of the possible oxide compounds for sodium cathodes is  $Na_xCoO_2$ . Reversible phase transition of  $Na_xCoO_2$  takes place in Na-cells as was shown by Delmas et al. in 1981. Figure 2.2 shows three different crystal structures of  $Na_xCoO_2$ . Feasibility of P2- $Na_xCoO_2$ as a cathode material was demonstrated in an all solid-state Na-ion battery. Compounds including both Co and Mn together were also investigated. Other studied exide compounds are for example NaCrO<sub>2</sub>, NaNiO<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, MnO<sub>2</sub> and NaVO<sub>2</sub>. [16]



Fig. 2.2: Various crystal structures of Na<sub>x</sub>CoO<sub>2</sub>: (a) P2-Na<sub>x</sub>CoO<sub>2</sub>, (b) 03-Na<sub>x</sub>CoO<sub>2</sub>, (c) P3-Na<sub>x</sub>CoO<sub>2</sub> [29]

#### 2.2 Anode Materials

Research is not focused only on the new materials, but also on new forms of known materials (e.g. different types of carbon based materials) and the ways of their manufacturing. Important part of research is also compatibility of anode materials with various electrolytes and cathodes. Some of the materials for sodium-ion anodes are be described in this section.

#### 2.2.1 Carbon Based Compounds

Graphite anodes are the most common in lithium-ion batteries, but amount of sodium that can be stored in graphite is limited. Research on insertion properties of different carbon compound were made by Doeff et al. in 1993. The study was done using sodium cells with the solid electrolyte. The best results of sodium intercalation were obtained with Shawinigan black (NaC<sub>15</sub>) and petroleum coke (NaC<sub>30</sub>). On the other hand, graphite electrode can accommodate only small amount of sodium (NaC<sub>70</sub>). [16]

Another study, led by Thomas et al., focused on properties of graphite and carbon fibers in liquid electrolyte consisting of NaClO<sub>4</sub> dissolved in ethylene carbonate. The study showed that reversible intercalation is possible with this materials, but with high irreversible capacity associated with formation of passivation layer on the electrode surface. The higher irreversible capacity was observed for graphite because of the higher specific area. Reversible capacity of carbon fibers was 55 mAhg<sup>-1</sup> and 14 mAhg<sup>-1</sup> for graphite. Grinding of carbon fibers increased reversible capacity to 83 mAhg<sup>-1</sup> (equals to NaC<sub>26</sub>). Various studies were made with different forms of carbon as anode material together with different types of cathodes and electrolytes. Some of them showed quite good reversible capacity, but usually with one or more disadvantages like low current rates, small number of cycles or need of elevated temperature. [16]

#### 2.2.2 $Na_x Ti_y O_z$ Based Compounds

Layered NaTiO<sub>2</sub> is one of the materials that can be used for anodes manufacturing. Achievable reversible capacity of NaTiO<sub>2</sub> anode is approximately  $152 \text{ mAhg}^{-1}$  at C/10 rate according to experiments of Di Wu et al [29]. It has excellent cyclability with almost 98 % of original capacity after 60 cycles. It is also characterised by the good rate capability. [29]

Figure 2.3 shows different anode materials for Na-ion batteries and their properties (reversible capacity, average voltage vs Na/Na<sup>+</sup>, specific energy density and cyclability). A can be seen, most of the materials contain titanium. Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> has good initial capacity but poor cyclability. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> has lower capacity, but it has good cyclability with carboxymethylcellulose binder. Excellent cyclability performs P2-Na<sub>0.66</sub>[Li<sub>0.22</sub>Ti<sub>0.78</sub>]O<sub>2</sub> compound that has negligible volume change 0.77 % during sodium insertion and extraction. [29]

O3-type NaTiO<sub>2</sub> can be synthesized for example by a solid-state reaction. Initial reagents are anatase (one of the mineral forms of  $TiO_2$ ) and sodium. This reagents, with



Fig. 2.3: Overview of anode materials for Na-ion batteries and their properties [29]

10% excess of sodium, are placed in stainless steel tube in a glove box filled with argon. The tube is sealed and fired at 920 °C for 12 hours i a flow of argon gas. Tube is opened in the glove box after cooling. NaTiO<sub>2</sub> is then mixed with conductive agent (e.g. carbon black Super P), binder (e.g. polyethylenetetrafluoride) in given weight ratio (e.g. 80:15:5) to make an anode mixture. [29]

 $Na_2Ti_6O_{13}$  can be also manufactured via a solid state reaction of  $TiO_2$  and  $Na_2CO_3$ . Mixture of those compounds is calcined at 800 °C for 20 hours. The mixture is than ground, mixed, pelletized and calcined again at 800 °C for 20 hours.  $Na_2Ti_6O_{13}$  has structure that is suitable for intercalation reactions, but it has low capacity for sodium insertion (capacity for lithium insertion is much higher). Figure 2.4 shows the channel structure of  $Na_2Ti_6O_{13}$  (pink spheres are sodium ions). [8]



Fig. 2.4: Structure of Na<sub>2</sub> Ti<sub>6</sub> O<sub>13</sub> [8]

#### 2.2.3 Transition Metals Conversion Compounds

Conversion principle is shown in figure 1.7 in the first chapter. Conversion reaction for sodium can be described by the equation

$$nNa^{+} + ne^{-} + M^{n+}X = Na_nX + M^0$$
 (2.5)

where M is a transition metal, n is the oxidation number of the transition metal ion, and X is an anion. Advantage of conversion compounds is their high theoretical capacity because multiple electron reaction is possible for each transition metal ion. Spinel NiCo<sub>2</sub>O<sub>4</sub> is one of the conversion compounds that were studied. Its theoretical capacity is approximately 890 mAhg<sup>-1</sup> [16]. This value is based on the assumption that 8 sodium ions can react with one NiCo<sub>2</sub>O<sub>4</sub>. Products of this conversion reaction are 2 atoms of Co, 1 atom of Ni and 4 molecules of Na<sub>2</sub>O. Specific capacity of approximately 250 mAhg<sup>-1</sup> was obtained using the full cell with NiCo<sub>2</sub>O<sub>4</sub> and Na<sub>0.7</sub>CoO<sub>2</sub> electrodes. Sulphide compounds (e.g. FeS<sub>2</sub> or Ni<sub>3</sub>S<sub>2</sub>) were also investigated. Compounds FeO, CoO and NiO are not suitable for the sodium-ion batteries in spite of excellent performance in the lithium-ion batteries. [16]

#### 2.2.4 Alloying Compounds

Alloying compounds are such compounds that can form alloys with sodium. Alloying principle in Li-ion batteries is schematically shown in figure 1.7 in the first chapter. One of the alloying compounds for sodium is  $Sb_2O_4$ . It has very high theoretical specific capacity 1227 mAhg<sup>-1</sup> because one unit of  $Sb_2O_4$  can accommodate 14 sodium ions. Achieved reversible capacity was 896 mAhg<sup>-1</sup>. [16]

The most significant problem of alloying compounds is very high volume change during charging and discharging. It is even worse than in Li-ion batteries because of the larger ionic radius of sodium. Acquiring the same capacity as conventional graphite electrode in Li-ion batteries would cause 150% volume expansion of the sodium alloying compound. [16]

#### 2.3 Electrolytes

Basically, there are two types of electrolytes from the solvent point of view: aqueous and non-aqueous. Non-aqueous are used more often. The most commonly used are salts NaClO<sub>4</sub> and NaPF<sub>6</sub> dissolved in propylene carbonate.[10] Different additives and solvents are studied to improve electrolyte performance with different electrodes. Aqueous electrolytes use water as solvent. Professor Jay Whitacre from Carnegie Mellon University developed aqueous hybrid ion battery in 2008. Both aqueous and non-aqueous electrolytes are investigated to improve their properties and to make them suitable for the commercial applications. [10] Table 2.6 shows few examples of used electrolytes in studies of different research groups. Electrolyte in all articles was 1 M solution of salt in solvent. In some cases, smaller amount (e.g. 5%) of fluorethylene carbonate (FEC) is used to improve performance of the battery [17].

Article Title	Salt	Solvent
High cyclability of carbon-coated TiO <sub>2</sub> nanoparticles	NaClO.	EC+DMC
as anode for sodium-ion batteries [11] NaClO <sub>4</sub>		1:1
Carbon-coated $Li_4Ti_5O_{12}$ nanowires showing		
high rate capability as an anode material for	NaClO <sub>4</sub>	$\mathbf{PC}$
rechargeable sodium batteries [15]		
Synthesis and electrochemical sodium and lithium		FC+DC
insertion properties of sodium titanium oxide with	$NaClO_4$	1.1
e tunnel type structure [14]		1.1
Introducing a 0.2 V sodium-ion battery anode:	NaClO	EC+PC
The $Na_2Ti_3O_7$ to $Na_3$ - $xTi_3O_7$ pathway[25]	NaClO4	1:1
Effect of surface modification on high-surface-area	NaClO	EC+DEC
arbon nanosheets anode in sodium ion battery [28] $[128]$		1:1

Tab. 2.6: Table of electrolytes used in different articles

#### 3 ANALYSIS METHODS

#### 3.1 Cyclic Voltammetry

Voltammetry is one of the most common methods for electrochemical analysis of electrodes not only for lithium-ion and sodium-ion batteries. It is based on the applying changing voltage to the test cell. Applied voltage and corresponding measured current is usually plotted to the I-V graph.

There are different types of voltammetry varying in the waveform of applied voltage. In potential step voltammetry, voltage is changed instantaneously and the current response to this step is measured. Another type is linear sweep voltammetry. Applied voltage is increased with given linear slope from one limit to the other limit. Current is measured simultaneously during the voltage sweep.

The most common method used for electrochemical characterisation of Li-ion and Na-ion batteries is cyclic voltammetry (CV). It is similar to the linear sweep, but after reaching the upper limit, voltage starts to decrease with the same rate towards the lower limit. This cycle can be repeated many times to analyse the repeatability of the chargedischarge process. One cycle of the CV is shown in figure 3.1. There is linear voltage increase from  $V_1$  to  $V_2$  followed by decrease with the same slope to the initial voltage. Current-voltage graph is usually characterised by one current peak in each direction ( $I_p^c$  and  $I_p^a$ ). This current peaks appear at two different potentials  $E_p^c$  and  $E_p^a$ .



Fig. 3.1: One cycle of cyclic voltammetry: voltage-time and current-voltage graph[2]

Key parameters of the cyclic voltammetry are lower an upper voltage limit, scan rate (slope of the voltage-time graph) and number of cycles. All those parameters influence the shape of the CV characteristics. Measuring of the multiple cycles reveals repeatability of the process. Typical is irreversible capacity loss during the first cycles because of the formation of solid electrolyte interface. Further capacity loss is caused by the material degradation process.

The value of current density for the current maximum  $(I_p^c \text{ and } I_p^a)$  in the I-V graph of CV can be described by the Randles-Sevcik equation fro reversible electrochemical processes:

$$i_p = 0.4463nFAC \left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$
(3.2)

where  $i_p$  is current maximum, n is number of electrons transferred in the redox event, F is Faraday constant, A is electrode area, C is diffusion coefficient, v is scan rate, D is diffusion coefficient, R is gas constant and T is thermodynamic temperature. According to this equation, current maximum increases with the square root of the scan rate in case of diffusion controlled process ). There is also surface accumulation of charge on a double layer. Current maximum increase due to this process is linear. [32] Influence of the scan rate on current maximum is shown in figure 3.3. According to the Randles-Sevcik equation, current maximum is decreasing with the square root of thermodynamic temperature.



Fig. 3.3: Scan rate influence on the I-V graph of cyclic voltammetry

Electrochemical test cell ECC-ref (manufactured by ELL-CEL<sup>®</sup>) was used for both cyclic voltammetry and galvanostatic cycling with potential limitation. This cell enables 2-electrode or 3-electrode operation when using the reference electrode.



Fig. 3.4: Electrochemical Test Cell ECC-ref [9]

## 3.2 Galvanostatic Cycling With Potential Limitation (GCPL)

Galvanostatic cycling is method equivalent to the charging and discharging of the cell with the constant current. The analysed cell is protected against damage during charging and discharging by the potential limitation. This method is used for measuring of the amp-hour capacity of the electrode (or the active material of the electrode). [32]

Transfered charge is given by the equation:

$$Q = \int_0^t I(t)dt \tag{3.5}$$

where Q is charge, and I(t) is a time function of the current passing threw the circuit. To make the value of transferred charge (electrode capacity) comparable, specific capacity (typically in mAhg<sup>-1</sup>) is usually used. It is given by dividing the capacity by the mass of the active material:

$$Q_{spec} = \frac{Q}{m_{active}} \tag{3.6}$$

The basic parameters of the galvanostatic cycling are charging current, discharging current and potential limits (determining boundary conditions of charged and discharged cell). Galvanostatic cycling can also be limited by the charge/discharge time or total charge. Current for charging and discharging is often given in "C" units instead of amps. This unit is linked to the capacity of the cell. 1C means that the capacity of the cell is fully charged in 1 hour. [32]

Measured characteristics are often plotted as charging/discharging characteristics. They show the dependence of the delivered or taken current on the cell voltage. Less used evaluation method is based on dependence of the cell voltage on time. [32]

#### 3.3 X-Ray Diffraction Spectroscopy

X-ray diffraction spectroscopy (XRD) is non-destructive technique for studying crystalline materials. The X-ray can interact with such materials and form diffraction patterns that are unique for different materials. It is possible to determine not only composition of the sample, but also the presence of different phases.

The smallest element forming the crystals is called a unit cell. It is described by three axis (a, b, c) and angles between them  $(\alpha, \beta, \gamma)$ . The distance of atoms in the unit cell depends on the composition and can be different in each direction. The principle of the X-ray diffraction can be described using two parallel planes (p1, p2) with atoms as a 2D model of crystal planes (figure 3.7). The distance of the planes is marked as d. Incidents rays (b1, b2) are approaching the crystal planes with the same angle  $\theta$ . Beam b1is reflected by the p1 plane and beam b2 is reflected by the p2 plane. Angles of the reflected rays are  $\theta'$  (same in size as  $\theta$ ). Diffraction of the reflected rays depends on the angle of incidence, distance of planes and wavelength of the X-ray.



Fig. 3.7: Principle of X-ray diffraction

The diffraction maximum occurs if the reflected rays meet in phase. It means that their path difference is equal to the integer multiple of their wavelength. This condition is described by the Bragg's law:

$$2d \cdot \sin\theta = n\lambda \tag{3.8}$$

where d is distance of the crystal planes,  $\theta$  is angle of the incident rays, n is integer and  $\lambda$  is wavelength.

XRD sample is usually a single crystal or polycrystalline sample (powder). It is important to have a smooth plane surface when analysing a powder. It is appropriate to grind the sample to particles of about 0.002 mm to 0.005 mm. Prepared powder is then pressed into the sample holder. [27]

The measurements in this work were done by Rigaku MiniFlex X-ray diffractometer with Cu X-ray source ( $\lambda(K\alpha) = 0.154$  nm) with Ni K $\beta$  filter. In this type of XRD analyser, x-ray tube is stationary, sample moves by the angle theta and the detector moves by the angle 2-Theta. Measured spectra is usually plotted as reflected intensities versus the detector angle (usually 2-Theta). The final spectra is compared with the database of standard samples to evaluate the results. The database is maintained by The International Centre for Diffraction Data (ICDD). [27]

#### 3.4 Scanning electron microscopy

Scanning electron microscope (SEM) is usually used when resolution of the optical microscope is not sufficient. Higher resolution of electron microscope is determined by the wavelength of accelerated electrons, that is much shorter than wavelength of visible light used in conventional optical microscopes. The highest achievable resolution of SEM is usually few nanometers.

Accelerating voltage used for imaging is usually from 1 kV to 30 kV. For some applications, accelerating voltage of few hundred volts can also be used (smaller interaction volume and sample damage). Interaction of electron beam with the sample generates various signals (see fig. 3.9). Each of them carries specific information about the sample and they are detected by different detectors (one detector can be able to detect one or more signals). The most often used signals are secondary electrons (SE) and backscattered electrons (BSE).

Secondary electrons (mostly used for evaluation of the samples in this work) carries information about topography of the sample surface. The flat parts of the sample generate less signal (are darker in the image) than edges. The maximum energy of secondary electrons was set to 50 eV. Backscattered electrons come from larger interaction volume and have large energy (from 50 eV up to energy of primary electrons). They carry information mostly about the atomic number. The signal strength (number of backscattered electrons) is rising with increasing atomic number (e.g. titanium looks brighter than aluminum).

The comparison of SE and BSE image is shown in figure 3.10. These pictures were taken by the Everhart-Thornley detector (ETD). This detector has a grid in front of it. Applied potential to the grid determines mode of the detector. Positive potential on the grid attracts low energy secondary electrons and detector works in SE mode (BSEs are detected too, but have minor affect on the final image). As can be seen in figure 3.10, the brightest parts of the tin spheres are edges. In BSE mode, negative potential is applied to the grid. This potential repels SEs, but is not high enough to repel high energy BSEs. Final image is formed of BSEs that are moving in the direction of the detector. In the ideal



Fig. 3.9: Electron interaction with matter [7]

BSE image, spheres would have one shade of grey. The placement of the detector causes them to be brighter from one side (direction of the detector) and darker from the other.



Fig. 3.10: Tin spheres on carbon in BSE (left) and SE (right) mode of Everhart-Thornley detector

#### 4 CHARACTERISATION OF TiO<sub>2</sub> SAMPLES

#### 4.1 TiO<sub>2</sub>-B Nanowires

This sample of TiO<sub>2</sub>-B was prepared according to the article "TiO<sub>2</sub>-B nanowires as negative electrodes for rechargeable lithium batteries" written by A. Robert Armstrong et al. [3]. This material was not synthesized within this thesis, it was only used for electrode preparation and evaluation. Initial components for the synthesis were anatase form of TiO<sub>2</sub> and 15 M aqueous solution of NaOH.

Figure 4.1 shows electrode made of TiO<sub>2</sub>-B nanowires before pressing. It is apparent that the size of particles is not uniform and that there also bigger conglomerations. After pressing the electrode by 50 kN (figure 4.2), its surface is much more flatter and compact. Electrochemical measurements were made in 2 electrochemical test cells (2 samples of electrodes). Fibreglass separator, 200  $\mu$ l of 1 M solution of NaClO<sub>4</sub> in EC+DMC (1:1) and disc of metal sodium were used to form each cell (this configuration and materials were used for all measurements in this work if not stated otherwise).



Fig. 4.1: TiO<sub>2</sub>-B nanowires - electrode before pressing



Fig. 4.2:  $TiO_2$ -B nanowires - electrode after pressing (50 kN)

#### 4.1.1 TiO<sub>2</sub>-B Nanowires: Cell 1 Measurements

Graphs in this section are arranged in the chronological order and open circuit voltage (OCV) graph is part of the appendix (same for all other sets of measurements).

The first graph 4.3 shows the cyclic voltammetry (CV) with voltage ramp 2 mV/s. As can be seen, there are no peaks showing electrode reaction. The maximum absolute value of current decreases from approximately 245 mA/g (first cycle) down to 145 mA/g (last cycle). Maximum of the second CV graph 4.4 with voltage ramp 0.1 mV/s is 30 mA/g.

Galvanostatic cycling with potential limitation is shown if figures 4.5 and 4.5. The maximum discharge capacity was 18.7 mAh/g (measured in the first cycle). Capacity was decreasing in the following cycles. Current used for the GCPL was 0.81 C (based on the first discharge cycle capacity).


Fig. 4.3: TiO<sub>2</sub>-B nanowires (cell 1) - cyclic voltammetry 2 mV/s



Fig. 4.4: TiO<sub>2</sub>-B nanowires (cell 1) - cyclic voltammetry 0.1 mV/s



**Fig. 4.5:** *TiO*<sub>2</sub>-*B* nanowires (cell 1) - *GCPL*: *I*=0.1 mA (equals 0.81 C)



**Fig. 4.6:** *TiO*<sub>2</sub>-*B nanowires* (*cell* 1) - *GCPL: I*=0.1 *mA* (*equals* 0.81 *C*)

## 4.1.2 TiO<sub>2</sub>-B Nanowires: Cell 2 Measurements

The shape of the CV graphs 4.7 and 4.8 was comparable to the firs cell measurements, but the absolute values of maximum current were higher (approximately 750 mA/g in the first cycle of 2 mV/s CV and 50 mA/g in the 0.1 mV/s CV). The last CV 4.11 was measured at the end. It was measured from 0 V to 4.2 V and maximum current was approximately 150 mA/g.



The highest capacity measured by GCPL was 26.2 mAh/g (fugure 4.9). The discharging current was 0.67 C.

Fig. 4.7: TiO<sub>2</sub>-B nanowires (cell 2) - cyclic voltammetry 2 mV/s



Fig. 4.8: TiO<sub>2</sub>-B nanowires (cell 2) - cyclic voltammetry 0.1 mV/s



**Fig. 4.9:** *TiO*<sub>2</sub>-*B* nanowires (cell 2) - *GCPL*: *I*=0.1 mA (equals 0.67 C)



Fig. 4.10: *TiO*<sub>2</sub>-*B* nanowires (cell 2) - *GCPL*: *I*=0.1 mA (equals 0.67 C)



Fig. 4.11: TiO<sub>2</sub>-B nanowires (cell 2) - cyclic voltammetry 2 mV/s

## 4.2 TiO<sub>2</sub>(B) KTO3.5 OP3 500

This monoclinic TiO<sub>2</sub>(B) was prepared (not within this thesis) by calcinition of hydrated potassium alkaline titanate. Used potassium titanate  $K_2Ti_4O_9$  was prepared from molar ratio of precursors 1:3.5. The sample underwent three cycles of protonization ionic exchange cycles. Calcination was done in the preheated furnace for 1 hour at 500 °C. Content of residual potassium in the titanate was 1.39 % (measured by atomic absorption spectroscopy). It means that 92.7 % of initial potassium was exchanged. [32]

The figure 4.12 shows electrode prepared from monoclinic  $\text{TiO}_2(B)$  (80 %), super P conductive carbon (10 %) and NMP binder (10 %) before pressing. The sample was tilted to 50 ° to emphasize the surface structure. Surface of pressed electrode (50 kN) is much flatter as can be seen in figure 4.13. Comparison of electrode before and after pressing with lower magnification is shown in figure 4.14, where the unevenness caused by the pressing tool is apparent.

Electrochemical measurements were made in 2 electrochemical test cells (2 samples of electrodes). Two pieces of fibreglass separator, 400  $\mu$ l of 1 M solution of NaClO<sub>4</sub> in EC+DMC (1:1) and a disc of metal sodium were used to form each cell.



Fig. 4.12:  $TiO_2(B)$  KTO3.5 OP3 500 - electrode before pressing (tilt 50°)



Fig. 4.13:  $TiO_2(B)$  KTO3.5 OP3 500 - electrode after pressing (tilt 50°)



**Fig. 4.14:**  $TiO_2(B)$  KTO3.5 OP3 500 - comparison of electrode before (left) and after (right) pressing (tilt 50°)

### 4.2.1 TiO<sub>2</sub>(B) KTO3.5 OP3 500: Cell 1 Measurements

The CV graph 4.15 has no current peaks showing electrode insertion/extraction activity (change of lower potential limit during measurement was probably caused by the software bug). The maximum current was approximately 250 mA/g in the firs CV and 22 mA/g in the second CV (graph 4.16) with voltage ramp 0.1 mV/s.

The maximum discharge capacity of the electrode during the GCPL with current 0.76 C was 25.1 mAh/g (the third cycle). The capacity was approximately 22.5 mAh/g in the first cycle and was slightly increasing during following cycles. The other GCPL (figures 4.19 and 4.18) was done with higher current (2.6 C) and maximum discharge capacity was 28.1 mAh/g.



Fig. 4.15: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - cyclic voltammetry 2 mV/s



Fig. 4.16: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - cyclic voltammetry 0.1 mV/s



Fig. 4.17: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - GCPL: I=0.1 mA (equals 0.76 C)



Fig. 4.18: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - GCPL: I=0.1 mA (equals 0.76 C)



Fig. 4.19: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - GCPL: I=0.4 mA (equals 2.6 C)



Fig. 4.20: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - GCPL: I=0.4 mA (equals 2.6 C)

### 4.2.2 TiO<sub>2</sub>(B) KTO3.5 OP3 500: Cell 2 Measurements

The shape of the CV graphs is similar to the first cell measurements. Cyclic voltammetry was done with 2 mV/s (graphs 4.21 and 4.23) and 0.1 mV/s (graphs 4.22 and 4.24) voltage ramp and two different voltage limits.

Two sets of GCPL measurements were done with 0.91 C and 3.83 C discharge current. The highest measured capacity was 16.1 mAh/g.



Fig. 4.21: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 2) - cyclic voltammetry 2 mV/s



Fig. 4.22: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 2) - cyclic voltammetry 0.1 mV/s



Fig. 4.23: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 2) - cyclic voltammetry 2 mV/s



Fig. 4.24: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 2) - cyclic voltammetry 0.1 mV/s



Fig. 4.25: *TiO*<sub>2</sub>(*B*) *KTO*3.5 *OP*3 500 (cell 2) - *GCPL*: current 0.1 mA (equals 0.91 C)



Fig. 4.26: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 2) - GCPL: current 0.1 mA (equals 0.91 C)



Fig. 4.27: *TiO*<sub>2</sub>(*B*) *KTO3.5 OP3 500 (cell 2)* - *GCPL: current 0.45 mA (equals 3.83 C)* 



Fig. 4.28: *TiO*<sub>2</sub>(*B*) *KTO3.5 OP3 500 (cell 2)* - *GCPL: current 0.45 mA (equals 3.83 C)* 

# 5 PREPARATION AND CHARACTERISATION OF SODIUM TITANATE CUBOID

Hydrothermal method of sodium titanate cuboid preparation was chosen because it had good performance as anode material for sodium ion batteries in study of Yan Zhang et al. [31]. This work also served as manual for the preparation process.

The preparation process and used chemicals were slightly modified. 8 ml of 30% H<sub>2</sub>O<sub>2</sub> was mixed with 160 ml of 2.5 M NaOH and stirred for 15 minutes. 0.33 mol of titanium n-propoxide was added to the mixture and stirred for 30 minutes. Final mixture was poured into the teflon tube with magnetic stirrer and placed into the microwave autoclave. Temperature in the sealed tube was risen to 150 °C and held for 6 hours. The system was cooled naturally to the room temperature. Pressure and temperature in the autoclave can be seen in figure 5.1.



Fig. 5.1: Temperature and pressure in the autoclave during hydrothermal synthesis

Final suspension was centrifuged and rinsed in water and ethanol few times to reduce its basicity. After last centrifugation, liquid part was poured out and sodium titanate was placed on the Petri dishes for drying at 80 °C. Top layer of centrifuged sodium titanate was white and consisted of smaller particles (confirmed by the electron microscope images) and bottom part was light yellow and consisted of larger particles. The white and yellow parts were separated to evaluate the differences between them.

SEM Figures 5.2 and 5.3 show sodium titanate before calcination and there is no obvious difference between the white and yellow component.



Fig. 5.2: White sample of sodium titanate before calcination



Fig. 5.3: Yellow sample of sodium titanate before calcination

Both samples were calcined at 800 °C. White sample (fig. 5.4) formed smaller particles than yellow sample (fig. 5.5).



Fig. 5.4: White sample of sodium titanate - calcined at 800  $^{\circ}C$ 



Fig. 5.5: Yellow sample of sodium titanate - calcined at 800  $^{\circ}C$ 

To evaluate the influence of calcination temperature on the final structure of sodium titanate, mixture of white and yellow sample was calcined at 700  $^{\circ}$ C and 900  $^{\circ}$ C. It is apparent that lower calcination temperature means smaller particles of sodium titanate.



Fig. 5.6: Mixture of white and yellow sample of sodium titanate - calcined at 900  $^{\circ}C$ 



Fig. 5.7: Mixture of white and yellow sample of sodium titanate - calcined at 700  $^{\circ}C$ 

XRD analysis was done with samples prepared by the synthesis. Figure 5.8 shows measured patterns. All calcined samples contain  $Na_2Ti_3O_7$  and  $Na_2Ti_6O_{13}$  (other compounds were not quantitatively evaluated within this work). First two black symbols from the left mark peaks used for evaluation of ratio of those compounds (peaks with the highest intensity in the reference patterns). Evaluation method was based on the comparison of area under those peaks. Other triangles show chosen peaks of  $Na_2Ti_3O_7$  to point out the different amount of it in the samples.



Fig. 5.8: X-ray diffraction patterns - first synthesis

Two other synthesis were done to obtain a sample with higher content of  $Na_2Ti_6O_{13}$ . For the second synthesis, the time in microwave autoclave was doubled to 12 hours. All other parameters were unchanged. According to the XRD analysis (graph 5.9), the change of time parameter didn't influenced the ratio of compounds in the sample.



Fig. 5.9: X-ray diffraction patterns - second synthesis

The last synthesis was dome with excess of titanium (0.24 mol of Ti, 0.104 mol of Na) to reduce formation of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. The amount of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> was decreased (graph 5.10) by this step, but some amount of TiO<sub>2</sub> was present in the synthesized sample (quantity was not evaluated within this work).



Fig. 5.10: X-ray diffraction patterns - third synthesis

Table 5.11 shows overview of  $Na_2Ti_3O_7$ :  $Na_2Ti_6O_{13}$  ratio in the synthesized sodium titanate samples. The calcination was done in the furnace where temperature was risen

 $3 \,^{\circ}C/min$  and the temperature (second column) was held for the given time (third column). The sample was cooled naturally in the furnace. Only sample from second synthesis calcined at 700  $^{\circ}C$  was placed into preheated oven and taken out after 3 hours. As can be seen in the table, the shortened time and placing into preheated oven had no effect on the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> : Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> ratio in comparison with sample from the first synthesis with the same calcination temperature.

The ratio of compounds was determined using the XRD analysis software. The approximate values were calculated from the area under peaks marked by the black triangle  $(Na_2Ti_3O_7)$  and the black circle  $(Na_2Ti_6O_{13})$  in the XRD graphs (5.8, 5.9, 5.10).

Sample	Calcination temp.	Calcination time	$\mathbf{Na}_{2}\mathbf{Ti}_{3}\mathbf{O}_{7}:\mathbf{Na}_{2}\mathbf{Ti}_{6}\mathbf{O}_{13}$
	$(^{\circ}\mathbf{C})$	(h)	(Ratio)
Synthesis 1	700	4	19:81
white + yellow			
Synthesis 1	800	1	$43 \cdot 57$
white	600	Ť	
Synthesis 1	800	4	46:54
yellow			
Synthesis 1	900	4	47 : 53
white + yellow			
Synthesis 2	800	4	42 : 58
white			
Synthesis 2	800	1	$45 \cdot 55$
yellow		Ĩ	-10.00
Synthesis 2	700	2*	$20 \cdot 80$
white + yellow	100		20.00
Synthesis 3	800	4	1:99
white			

Tab. 5.11: Quantification of XRD measurements

\* Sample was placed in preheated furnace and taken out after 3 hours.

Electrochemical measurements were made in 4 electrochemical test cells (2 samples of white titanate and 2 samples of yellow titanate electrodes). Fibreglass separator, 200  $\mu$ l of 1 M solution of NaClO<sub>4</sub> in EC+DMC (1:1) and disc of metal sodium were used to form each cell.

### 5.0.1 Measurements with White Titanate 800 °C: Cell 1 Measurements

The first GCPL was done with 11.1 C current (5.12) and the discharge capacity did not exceed 15 mAh/g with this discharge current. The results with lower currents were better and capacity during the first discharge cycle of measurements with 0.31 C and 0.06 C current was above 60 mAh/g (graphs 5.14 and 5.16). Discharge capacity was between 13 and 15 mAh/g for the 4.5 C measurement. Last GCPL was done with the same current (0.1 mA) as the second measurement, but the capacity fell down to less than a half.

Two CV measurements were made at the end. The graphs (5.22 and 5.23) did not show any significant current peak.



**Fig. 5.12:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.5 mA (equals 11.1 C)



Fig. 5.13: Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.5 mA (equals 11.1 C)



Fig. 5.14: Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.1 mA (equals 0.31 C)



**Fig. 5.15:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.1 mA (equals 0.31 C)



**Fig. 5.16:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.02 mA (equals 0.06 C)



**Fig. 5.17:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.02 mA (equals 0.06 C)



Fig. 5.18: Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.34 mA (equals 4.5 C)



**Fig. 5.19:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.34 mA (equals 4.5 C)



**Fig. 5.20:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.1 mA (equals 0.74 C)



**Fig. 5.21:** Sodium titanate HT1, 800 °C, white (cell 1) - GCPL: I=0.1 mA (equals 0.74 C)



Fig. 5.22: Sodium titanate HT1, 800 °C, white (cell 1) - cyclic voltammetry 2 mV/s



Fig. 5.23: Sodium titanate HT1, 800 °C, white (cell 1) - cyclic voltammetry 0.1 mV/s

#### 5.0.2 Measurements with White Titanate 800 °C: Cell 2 Measurements

Cyclic voltammetry was done before the GCPL for this cell. The first was done with 2 mV/s (5.24) and shows two peaks for positive current (at approx. 0.3 V and 0.95 V) and one for negative current (at approx. 0.7 V). Position of the peak is slightly different for the second CV (5.25) and there is one more peak for the positive current.

The highest measured capacity was almost 90 mAh/g (5.26). Discharge capacity of the electrode was decreasing during other GCPL measurements. Even if the current was lowered from 0.48 C to 0.2 C (graphs 5.28 and 5.30), capacity did not increase.

Last two CV graphs (5.32, 5.33) have the same parameters as the first two CV graphs from this series (5.24, 5.25), but there are no current peaks. The change is probably caused by the degradation of the electrode.



Fig. 5.24: Sodium titanate HT1, 800 °C, white (cell 2) - cyclic voltammetry 2 mV/s



Fig. 5.25: Sodium titanate HT1, 800 °C, white (cell 2) - cyclic voltammetry 0.1 mV/s



**Fig. 5.26:** Sodium titanate HT1, 800 °C, white (cell 2) - GCPL: I=0.02 mA (equals 0.03 C)



**Fig. 5.27:** Sodium titanate HT1, 800 °C, white (cell 2) - GCPL: I=0.02 mA (equals 0.03 C)



Fig. 5.28: Sodium titanate HT1, 800 °C, white (cell 2) - GCPL: I=0.2 mA (equals 0.48 C)



**Fig. 5.29:** Sodium titanate HT1, 800 °C, white (cell 2) - GCPL: I=0.2 mA (equals 0.48 C)



**Fig. 5.30:** Sodium titanate HT1, 800 °C, white (cell 2) - GCPL: I=0.07 mA (equals 0.2 C)



**Fig. 5.31:** Sodium titanate HT1, 800 °C, white (cell 2) - GCPL: I=0.07 mA (equals 0.2 C)



Fig. 5.32: Sodium titanate HT1, 800 °C, white (cell 2) - cyclic voltammetry 2 mV/s



Fig. 5.33: Sodium titanate HT1, 800 °C, white (cell 2) - cyclic voltammetry 0.1 mV/s

### 5.0.3 Measurements with Yellow Titanate 800 °C: Cell 1 Measurements

The CV graphs 5.34 and 5.35 have the similar shape as the graphs of white titanate, including the peak positions. Only the current values are lower.

The first GCPL (graph 5.36) shows quite stable discharge capacity around 62.5 mAh/g with 0.22 C current. Lowering the current to 0.11 C leads to capacity increase to capacity 63 mAh/g (graph 5.38). The highest discharge capacity 77 mAh/g was measured during 0.04 C discharge cycle (graph 5.40). Increasing the current to 1.25 C lead to the capacity drop to 25 mAh/g (graph 5.42). The last GCPL was done with 0.27 C current and the maximum capacity was 41 mAh/g.



Fig. 5.34: Sodium titanate HT1, 800 °C, yellow (cell 1) - cyclic voltammetry 2 mV/s



Fig. 5.35: Sodium titanate HT1, 800  $^{\circ}C$ , yellow (cell 1) - cyclic voltammetry 0.1 mV/s



**Fig. 5.36:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.085 mA (equals 0.22 C)



**Fig. 5.37:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.085 mA (equals 0.22 C)



**Fig. 5.38:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.045 mA (equals 0.11 C)



**Fig. 5.39:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.045 mA (equals 0.11 C)


**Fig. 5.40:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.02 mA (equals 0.04 C)



Fig. 5.41: Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.02 mA (equals 0.04 C)



Fig. 5.42: Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.2 mA (equals 1.25 C)



Fig. 5.43: Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.2 mA (equals 1.25 C)



**Fig. 5.44:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.07 mA (equals 0.27 C)



**Fig. 5.45:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.07 mA (equals 0.27 C)

#### 5.0.4 Measurements with Yellow Titanate 800 °C: Cell 2 Measurements

First GCPL measurements with this sample were done with high discharge current (slow charging by the low current at the beginning was probably the software bug). High discharge current (0.5 mA) resulted in the capacity lower than 5 mAh/g (graph 5.46).

Following cyclic voltammetry (graph 5.48) showed different shape in comparison with cell 1 measurements, probably because of the high current during GCPL.

The next GCPL was done with lower current (0.22 C) and the obtained capacity was around 33 mAh/g (graph 5.49). The last GCPL showed very poor capacity, that was lower than 1 mAh/g (graph 5.51).



**Fig. 5.46:** Sodium titanate HT1, 800 °C, yellow (cell 1) - GCPL: I=0.5 mA (equals 29.3 C)



**Fig. 5.47:** Sodium titanate HT1, 800 °C, yellow (cell 2) - GCPL: I=0.5 mA (equals 29.3 C)



Fig. 5.48: Sodium titanate HT1, 800 °C, yellow (cell 2) - cyclic voltammetry 2 mV/s



**Fig. 5.49:** Sodium titanate HT1, 800 °C, yellow (cell 2) - GCPL: I=0.025 mA (equals 0.22 C)



**Fig. 5.50:** Sodium titanate HT1, 800 °C, yellow (cell 2) - GCPL: I=0.025 mA (equals 0.22 C)



Fig. 5.51: Sodium titanate HT1, 800 °C, yellow (cell 2) - GCPL: I=0.34 mA (equals 166 C)



Fig. 5.52: Sodium titanate HT1, 800 °C, yellow (cell 2) - GCPL: I=0.34 mA (equals 166 C)

#### 5.0.5 Measurements with White Titanate without Calcination: Cell 1 Measurements

Measurements with the white sodium titanate without calcination were made to evaluate its properties and possibility of its use as an electrode material for sodium-ion batteries.

The cyclic voltammetry graphs 5.53 and 5.54 have no current peaks showing the electrode reaction and the current is decreasing in each cycle. The GCPL was done with the low current 0.13 C (0.02 mA) and the discharge capacity is 51 mAh/g (graph 5.55).



Fig. 5.53: Sodium titanate HT1, white without calcination (cell 1): cyclic voltammetry 2 mV/s



Fig. 5.54: Sodium titanate HT1, white without calcination (cell 1): cyclic voltammetry 0.1 mV/s



**Fig. 5.55:** Sodium titanate HT1, white without calcination (cell 1) - GCPL: I=0.02 mA (equals 0.13 C)



Fig. 5.56: Sodium titanate HT1, white without calcination (cell 1) - GCPL: I=0.02 mA (equals 0.13 C)

#### 5.0.6 Measurements with White Titanate without Calcination: Cell 2 Measurements

This cell with sodium titanate without calcination shows similar results as the first cell. There are no current peaks in the cyclic voltammetry graphs 5.57 and 5.57. The measured discharged capacity is 64 mAh/g.



Fig. 5.57: Sodium titanate HT1, white without calcination (cell 2): cyclic voltammetry 2 mV/s



Fig. 5.58: Sodium titanate HT1, white without calcination (cell 2): cyclic voltammetry 0.1 mV/s



**Fig. 5.59:** Sodium titanate HT1, white without calcination (cell 2) - GCPL: I=0.02 mA (equals 0.1 C)



Fig. 5.60: Sodium titanate HT1, white without calcination (cell 2) - GCPL: I=0.02 mA (equals 0.1 C)

#### CONCLUSION

The major aim of this work was to synthesize sodium titanate and to perform its characterisation with focus on electrochemical properties, composition and morphology. Electrochemical and morphological characterisation was done also with two  $TiO_2$  samples.

The samples from the first hydrothermal synthesis contained Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> and Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>. The ratio of those compounds varied from 19:81 to 47:53 according to the calcination conditions. According to the images from the electron microscope, lower calcination temperature results in smaller sodium titanate particles. Two other synthesis were made to get the sample with minimal amount of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. During the second synthesis, time in the microwave autoclave at 150 °C was doubled in comparison with the first synthesis. According to the following XRD analysis, this step had no effect on the Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>:Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> ratio. The third synthesis was done with excess of titanium (contained in titanium n-propoxide) to reduce the formation of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. The ratio of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>:Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> changed to approximately 1:99, but some amount of TiO<sub>2</sub> was present in the sample.

Electrochemical characterisation was done with the TiO<sub>2</sub>-B nanowires sample, monoclinic TiO<sub>2</sub>(B) KTO3.5 OP3 500 sample and with samples from the first hydrothermal synthesis. None of the prepared electrodes showed ideal characteristics for sodium-ion batteries. Table 5.61 summarizes the maximum discharge capacity for each sample of material. The highest capacity was obtained with the white sodium titanate sample from the first synthesis calcined at 800 °C. This sample (together with yellow titanate calcined at 800 °C) had current peaks in the cyclic voltammetry. All other samples had no current peaks in CV graphs indicating the electrode reaction. On the other hand, cyclability of synthesized samples calcined at 800 °C was poor (activity of electrodes disappeared during the measurements).

Sample	Current	Current	Max. Discharge
Sample	(uA)	(C)	Capacity (mAh/g)
TiO <sub>2</sub> -B Nanowires	100	0.67	26.2
TiO2(B) KTO3.5 OP3 500	400	2.6	28.1
White titanate 800 $^{\circ}C$	20	0.03	89.6
Yellow titanate 800 $^{\circ}\mathrm{C}$	20	0.04	77.3
White titanate without calcination	20	0.1	64.4

Tab. 5.61: Maximum measured discharge capacity for each material sample

There are few ways of trying to improve the performance of sodium titanate electrodes. One of them is to evaluate the effect of lower amount of  $Na_2Ti_3O_7$  in the sample (prepared by the third synthesis) or to prepare different sodium titanate compound. The other possibility could be coating of the sodium titanate particles by the thin carbon layer. Improvement could also be done by optimization of electrode composition (ratio of active material, binder and conductive carbon) and thickness. The last thing I would suggest is testing of different electrolytes and their influence on the electrode performance.

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## ABBREVIATIONS AND ACRONYMS

a-Si	amorphous Si
BSE	backscattered electron
c-Si	Crystalline Si
CV	Cyclic voltammetry
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DME	Dimethoxy ethane
EC	ethylene carbonate
ETD	Everhart-Thornley detector
FEC	fluorethylene carbonate
HF	hydrofluoric acid
ICDD	The International Centre for Diffraction Data
Li-ion	lithium-ion
$Li^+$	lithium ions
LCO	LiCoO <sub>2</sub>
LFP	${\rm LiFePO}_4$
LMO	$LiMn_2O_4$
LNM	$\rm LiNi_{1/2}Mn_{3/2}O_4$
LNO	$LiNiO_2$
LTO	Lithium titanate $(Li_4Ti_5O_{12})$
NMC	$\text{LiNi}_{y}\text{Mn}_{y}\text{Co}_{1-2y}\text{O}_{2}$
NMP	N-Methyl-2-pyrrolidone
NiCd	nickel cadmium
NiMH	nickel metal hydride
OCV	open circuit voltage
PC	propylene carbonate

SE	secondary electron
SEI	solid electrolyte interface
SEM	scanning electron microscope
SHE	standard hydrogen electrode
XRD	X-ray diffraction cpectroscopy
2Me-THF	2-Methyl-tetrahydrofuran
$\gamma ext{-BL}$	$\gamma$ -Butyrolactone

# LIST OF SYMBOLS

E	Volumetric or gravimetric density
$E_{WE}$	Potential of working electrode
Ι	Electric current
Q	Electric charge
$V_e$	Electrode potential
ε	Dielectric constant
$\mu$	Chemical potential

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#### APPENDIX

### Open circuit voltage graphs



Fig. 62: TiO<sub>2</sub>-B nanowires (cell 1) - open circuit voltage measurement



### **OCV** graphs

Fig. 63: TiO<sub>2</sub>-B nanowires (cell 2) - open circuit voltage measurement



Fig. 64: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 1) - open circuit voltage measurement



Fig. 65: TiO<sub>2</sub>(B) KTO3.5 OP3 500 (cell 2) - open circuit voltage measurement



Fig. 66: Sodium titanate HT1, 800 °C, white (cell 1) - open circuit voltage measurement



Fig. 67: Sodium titanate HT1, 800 °C, white (cell 2) - open circuit voltage measurement



Fig. 68: Sodium titanate HT1, 800 °C, yellow (cell 1) - open circuit voltage measurement



Fig. 69: Sodium titanate HT1, 800 °C, yellow (cell 2) - open circuit voltage measurement



Fig. 70: Sodium titanate HT1, white (cell 1) - open circuit voltage measurement



Fig. 71: Sodium titanate HT1, white (cell 2) - open circuit voltage measurement