5. Nanostructured materials and their thin films for Li-ion battery electrodes: synthesis, research and performance Nanostrukturēti materiāli un to plānās kārtiņas Li-jonu bateriju elektrodiem: sintēze, pētījumi un darbība

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5.1. Review of materials for Li-ion battery electrodes

After commercialization of Li-ion battery with metallic lithium anode and numerous self-ignition cases in hands of consumers, carbon-based anode for rechargeable batteries has been the preferred choice for the anode [1]. Here, carbon porous/layered structures are reversibly absorbing/desorbing lithium ions at low electrochemical potentials. Graphite can intercalate one Li atom per carbon ring: $\text{Li}^+ + \text{e}^- + \text{C}_6 \Rightarrow \text{LiC}_6$ corresponding to 372 mAh/g theoretically (comparing to about 3800 mAh/g for Li metal). Li can intercalate at an even higher capacity with some amorphous carbons, corresponding to a stoichiometry of LiC₃. Therefore, by replacing Li metal anodes with carbon nanomaterials in Li batteries, there is a 90% decrease of anode capacity, but the advantages are an increased stability and a prolonged cycle life [2].

The most important cathode materials for commercially available Li-ion batteries are layered oxides with 3.4-4 V potential (versus Li electrode) LiCoO₂, as well as LiMn₂O₄ [3], LiFePO₄ [4] and LiMn_xLi_yCo_zO₂ [5] with practically achievable capacities of 150, 120, 155 and 160 mAh/g, respectively.

As a rule, the electrodes are formed by mixing active material with various nanostructured carbon materials to improve the electrical and heat conductivities, as well as mechanical strength. In the last few decades, the number of the research articles on "nanostructured carbon materials" has grown exponentially. Nanoporous carbon materials (NCM) can be classified as various carbon allotropes in 0D (amorphous carbon black and graphitized carbon black), 1D (polymer chains), 2D (graphene) and 3D (diamond) scale. There are up to 100 review articles about their research in different applications (see, for example, [1, 6]). By assembling carbon nanomaterials with functional metal or oxide nanocrystals, composites with new functions in electrical, physical, or chemical properties are obtained. In this chapter our research results have been summarized based on the publications [1, 7–9] about the role and properties of nanostructured carbon materials in lithium ion batteries, electrodes for supercapacitors and hydrogen storage materials.

5.2. Methods for synthesizing materials and obtaining thin/thick films used in this research

A thin film is a thin layer of material, which has been obtained by depositing single atoms, molecules or ions [10]. A thin film is different from a thick film, which is obtained by reducing the size of a thick material or depositing readily-made grains or big clusters of atoms, molecules and ions. There are chemical and physical thin film deposition techniques. Physical techniques include mechanical, electromechanical or thermodynamic processes, while chemical thin film deposition techniques usually involve a liquid precursor that forms a thin solid film as a result of a chemical reaction or indifferent solution with dispersed nanopowder of material. The most popular physical thin film deposition techniques are physical vapour deposition (resistive, inductive, electron beam, pulsed laser, arc-discharge, etc.) and sputtering techniques (direct current, alternating current, impulse, etc.). The most typical thick film growth techniques include electrochemical anodation and deposition, electrophoretic deposition, spray pyrolysis, electrostatic spinning, spin coating and more. Below, we will describe the methods used in this study in greater detail. The thickness of the films was evaluated by using a Veeco Dektak 150 profilometer.

Pulsed laser deposition (PLD) is based on a target located in a vacuum chamber being irradiated with a high energy pulsed laser. As a result, the target atoms are being excited. Target ablation, surface exfoliation and plasma formation take place [11]. The products of pulsed laser - target interaction form a directed flow of particles towards the substrate. Part of the particles are deposited on the substrate and form a thin film. This technique is relatively easy to optimize and therefore is very popular for scientific purposes. In this research [9], pulsed laser deposition (PLD) ArF excimer laser with a wavelength of 248 nm was used for LiFePO4 thin film deposition by PLD. The energy of the laser beam in front of the lens of the vacuum chamber was 70-90 mJ, the area of the target irradiated by the laser - 4.5 mm². Laser frequency - 5 Hz, pulse length - 25 ns. The target material was LiFePO4 tablet that was prepared as described before. The initial vacuum in the vacuum chamber was 3.10⁻⁶ mBar. The chamber was then filled with argon to a pressure of 0.2 mBar, gas flow – 3 sccm/s. During the thin film deposition, the target rotation speed was 0.5 Hz. Before the thin film deposition, the target was pre-ablated with 600 laser pulses. During the thin film deposition, the substrate temperature was 500-530 °C. Thin films were deposited on Nb doped SrTiO3 (Nb:STO) monocrystals, Nb content - 0.5 wt.%, polished from one side, crystallographic orientation (100), size: 5×5 mm.

Magnetron sputtering is another popular physical vapour deposition technique [10]. Contrary to PLD, magnetron sputtering can easily be used to coat large surfaces. The technique is based on collisions between an inert gas and a target, which is made either from a pressed powder or a monolithic metal or alloy. We used a device made by Sidrabe, Inc. in direct current (DC) or radio frequency (RF) modes. Thin LiFePO₄ films were obtained in RF mode with frequency 13.56 MHz and discharge power 300 W. Target was prepared by pressing LiFePO₄ powder (two different materials were used – synthesized at Institute of Inorganic Chemistry (RTU) and commercial powder obtained from Linyi Gelon (New Battery Materials Co.) with 3.9 mPa pressure. The diameter of the target – 15 cm, distance between the target and substrate in sputtering chamber – 15 cm. Before deposition a pressure of $5 \cdot 10^{-5}$ mBar was obtained in the vacuum chamber. Argon was used as a sputtering gas, the target was presputtered for at least 10 min. In some cases, substrate was heated to 500 °C. Thin films were deposited on stainless steel, silicon monocrystals and glass substrates. In some cases, thin film recrystallization for 1 h at 600 °C in Ar was performed.

Electrophoretic deposition (EPD). EPD method is a highly beneficial, low-cost and ecofriendly technique for the preparation of required films and multi-layer coatings [8, 11]. For the electrophoretic growth two 3×3 cm² stainless steel (grade 316) electrodes were used. Distance between electrodes was 1 cm. A constant voltage of 100 V was applied between the electrodes by DC Power Supply (Agilent Technologies N5772A) and held for 10 min. EPD ensures colloidal particle deposition on substrate from electrically conductive electrolyte, in this case isopropanol. The process begins when applied electric field makes dispersed colloidal particles migrate to the electrode, where particles stay intact after losing charge. The deposited coatings were gradually heated (5 °C/min) and annealed at 500 °C for 2 h.

5.3. Characterization methods of synthesized materials and devices

Analysis of material composition, structure and morphology. The structure of research materials was analysed by XRD (Cu Ka radiation), morphology was studied by two different SEM (table-top device Phenom Pro; Zeiss Merlin; Tescan Lyra). Atomic force microscopy (AFM) was used in a contact mode, silicon needle with a radius smaller than 10 nm was used. Thin film thickness was determined by breaking the thin film and analysing the cross-section by SEM or by a focused ion beam (FIB) – gallium ions were used to etch a part of the thin film, the cross-section was then studied by SEM. To determine composition of samples the EDAX (Eagle 3) XRF spectrometer was used. Sample excitation by X-rays (Rh tube) focused by poly capillary fibre lens, minimum spot size 50 microns (fwhm). Energy dispersive liquid N₂-cooled Si detector with Be window, suitable for detecting of XRF of chemical elements ranging from Na to U. The composition of selected samples was analysed by ICP-OES. Thin film stoichiometry on the surface and in the bulk of the thin film was analysed by secondary ion mass spectroscopy (SIMS) by using 15 keV Ga⁺ ion gun. Selected samples (powders, thin films) were studied by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe) the spectra were obtained in a vacuum chamber with a pressure under $2 \cdot 10^{-10}$ Torr by using Al Ka X-rays with 1486.6 eV energy.

From spectroscopical methods to determine the structure, Raman spectroscopy was used (Renishaw InVia instrument with green laser (514 nm, max power 20 mW), objective \times 100, laser power used 100%, 30–4000 cm⁻¹ exposure time 10 s; red laser (633 nm, max power 12.5 mW) objective \times 100, laser power used 100%, 30–4000 cm⁻¹ exposure time 10 s).

Electrochemical measurements. LiFePO₄ thin film electrodes were measured in Swagelok-type two electrode electrochemical cells with a metallic lithium counter

electrode that was at the same time used also as a reference electrode. 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in volume ratio 1 : 1 was used as an electrolyte. Whatman GF/F glass microfiber separator was also used. Electrochemical impedance spectroscopy for LiFePO₄ thin films deposited with magnetron sputtering was carried out in a cell containing 1 M LiClO₄ in propylene carbonate as an electrolyte. Electrochemical cells were assembled in an argon-filled glove box. Electrochemical measurements were carried out with potentiostat Voltalab PGZ-301 and Solartron 1287A in combination with frequency analyser Solartron 1255. For LiFePO₄ thin films deposited by PLD, the electrolyte used was 1 M LiPF₆ in EC and diethylene carbonate (DEC) in volume ratio 1 : 1. Celgard 2500 polypropylene (PP) separator was also used. Electrochemical cells were assembled in an argon-filled glove box with O₂ and H₂O content lower than 1 ppm. Electrochemical measurements were performed by using potentiostats Voltalab PGZ-301, Voltalab PGZ-402, Autolab PGSTAT101 and Solartron 1287A in combination with frequency analyser Solartron 1255.

5.4. Thin film LiFePO₄ cathodes for Li ion batteries: characterisation, structure and composition, electrochemical properties

 $LiFePO_4$ is one of the most researched lithium ion battery cathode materials and considered to be a model material that serves to understand many basic phenomena taking place in lithium insertion materials. The prospects of improving the LiFePO₄ electrodes is still being actively studied [12–16]. However, several fundamental properties of the material, such as its particle-by-particle (de)lithiation behavior and phase-separation within the LiFePO₄ have remained elusive [12]. This chapter is based on ref. [9] and for more details the reader can be referred to the said work.

Thin films deposited by pulsed laser deposition

The XRD analysis of the prepared PLD target (Fig. 5.1.) indicates that the material is pristine $LiFePO_4$. This is additionally confirmed by ICP-OES measurements which corroborate that the target material is stoichiometric $LiFePO_4$ within the margin of error.



Figure 5.1. XRD pattern of LiFePO₄ powder and thin film deposited with PLD.

The XRD data for the obtained LiFePO₄ thin films also display only peaks characteristic to LiFePO₄. ICP-OES results show stoichiometry $Li_{0.94}Fe_{1.01}P_{0.99}O_{3.96}$, indicating a slight lithium loss during the thin film deposition.

The SEM images of the thin films (Fig. 5.2) indicate that the obtained thin films are composed of longitudinal particles with an average diameter of 5 μ m. These particles are composed of smaller grains with diameter of 50–500 nm as shown in Fig. 5.2. (b). The color of the grains in Fig. 5.2 is different due to variations in the crystallographic orientations. A few cracks can also be observed. Most likely, they are formed as a result of the substrate heating due to different thermal expansion coefficients of Nb:STO and LiFePO₄ [17–19].

Cross-sections of LiFePO₄ thin films can be seen in Fig. 5.2. (c) and (d). They indicate that the thin film is dense, with no significant pores and with a smooth surface. This is also confirmed by AFM. The roughness analysis by using AFM indicates the actual surface and projected surface of the sample to differ by only 2%. Thin film deposition rate was determined to be 200 nm/h.



Figure 5.2. LiFePO₄ thin film SEM (a), (b) surface and (c), (d) cross-section images

The discharge capacities of the obtained thin films are up to 118 mAh/g for the 100 nm thin film and slightly less for thicker thin films (see Fig. 5.3). 118 mAh/g constitute around 70% of the 170 mAh/g theoretical capacity of LiFePO₄. The capacities are very high when compared with other LiFePO₄ thin film studies [20–30]. All electrochemical measurements have been performed in two electrode electrochemical cells that were modified in order to avoid undesired side reactions connected with the electrolyte decomposition. At sufficiently small mass of active material the signal from such side reactions becomes significant.



Figure 5.3. Galvanostatic charge and discharge experiments for: (a) 100 nm, (b) 200 nm and (c) 300 nm thick LiFePO₄ thin films; (d) rate capabilities, (e) cyclability of a 200 nm thin film, (f) cyclic voltammetry curve, 1 C = 170 mA/g

The cyclability of the obtained LiFePO₄ thin films is very good -85% of the initial discharge capacity of a 200 nm thin film is retained after 100 charge and discharge cycles at 0.7 C rate (Fig. 5.3 (e)). Cyclic voltammetry (CV) curves display the peaks characteristic to lithium insertion and extraction (Fig. 5.3 (f)).

Electrochemical impedance spectroscopy (EIS) was performed for several LiFePO₄ thin films – see Fig. 5.4 (b). The charge transfer resistance increases with increasing LiFePO₄ thin film thickness, and the values of the charge transfer resistance are close to those of the expected electronic resistance of the thin film.

By using EIS and galvanostatic intermittent titration technique (GITT), the effective chemical diffusion coefficients of LiFePO₄ thin films were determined. Their values can be seen in Fig. 5.4. (b) and (c). For stoichiometries that are close to $\text{Li}_{0.5}\text{FePO}_4$, the effective chemical lithium diffusion coefficient D_{Li} is approximately 10^{-17} cm²/s. At higher and lower lithium concentrations the determined diffusion coefficients are larger. The effective chemical diffusion coefficients of lithium calculated from GITT data in intermediate states of charge are approximately 10^{-17} cm²/s and 10^{-16} cm²/s for calculations done by using charge and discharge data, respectively. The diffusion coefficients calculated from charge and discharge measurements differ because the thin film de-lithiation process has larger resistance (higher overvoltage) due to the electronic conductivity of FePO₄ being lower than for LiFePO₄ [31]. Additionally, since the thin film was deposited in a stoichiometry that is close to LiFePO₄ (and not FePO₄), during de-lithiation additional mechanical strains can develop, thus hindering lithium transport in the de-lithiated state. Diffusion coefficients calculated from EIS and GITT data are close and also in agreement with the values determined from the CV curves by using Randles – Sevcik equation (10^{-18} – 10^{-17} cm²/s).

Interpreting the calculated effective chemical diffusion coefficients, one has to take into account that, firstly, the model which is used for calculation of D_{Li} assumes that all particles are lithiating and de-lithiating at the same time, which might not be the case with LiFePO₄ [32]. Secondly, the aforementioned methods for calculating D_{Li} are intended for solid solutions and not for two-phase materials such as LiFePO₄. Therefore, the change in the free energy that comes from the separation of lithium rich and lithium poor phases is not taken into account [33]. Due to aforementioned reasons, the calculated results are called effective (or apparent) chemical diffusion coefficients, and they characterize not only the diffusion but also the overall lithium kinetics in the LiFePO₄ electrode.



Figure 5.4. (a) EIS results for LiFePO₄ thin films with various thicknesses; effective chemical lithium diffusion coefficients for a 200 nm LiFePO₄ thin film obtained by using (b) EIS and (c) GITT

Thin films deposited by magnetron sputtering

The LiFePO₄ thin films deposited by radio frequency magnetron sputtering are also composed of crystalline LiFePO₄. Fig. 5.5 shows SEM images of LiFePO₄ thin films obtained by magnetron sputtering. Distinct grains can be observed in the thin film with a size of 1–10 μ m. Although the grains are packed densely, grain boundaries can be clearly distinguished. No cracks are formed during the deposition, the surface adhesion is sufficient for the thin film to adhere to the substrate.



Figure 5.5. SEM images of LiFePO₄ thin films obtained by magnetron sputtering

CV curves in Fig. 5.6. (a) indicate that the best electrochemical properties can be obtained by annealing the thin film after its deposition. Annealing is important because the particles reaching the substrate during the deposition may not have sufficient energy to form ordered crystalline structures. The obtained capacities are up to 61 mAh/g at 0.1črate (17 mA/g) for a 1000 nm film (see Fig. 5.6. (b)). The capacities measured at higher charge and discharge rates are 30 mAh/g at 0.2 C, 19 mAh/g at 0.3 C and 10 mAh/g at 1 C.

Effective chemical diffusion coefficients of lithium are shown in Fig. 5.6. (c). The determined diffusion coefficients are by several orders of magnitude higher than the ones obtained for thin films deposited by PLD. However, these values are also in agreement with those reported in literature (in the range of 10^{-18} to 10^{-10} cm²/s [20, 34–36]. It must be noted again that the values of effective chemical diffusion coefficients are determined not only by lithium diffusion, but also by differences in electrode morphology, grain structure and composition.



Figure 5.6. (a) CV curves for various LiFePO₄ thin films (v = 1 mV/s), (b) galvanostatic charge and discharge curves for 1000 nm thin film, 1 C = 170 mA/g, (c) effective chemical diffusion coefficient of lithium in a LiFePO₄ thin film at various states of charge

Sequential particle charging and discharging in LiFePO₄ thin films

Measurements of voltage hysteresis were performed for LiFePO₄ thin films deposited by PLD. The measurements are based on a galvanostatic charge and discharge experiments in a limited charge interval. Open circuit voltage (OCV) is being measured between galvanostatic measurements. Voltage hysteresis measurements for Li_xFePO₄ were conducted in the lithium concentration range 0.1 < x < 0.9, where LiFePO₄ is expected to separate in lithium-rich and lithium-poor phases. The experimental procedure is schematically shown in Fig. 5.7. The measurement cycle demonstrated in the figure was repeated several times, the low currents used for hysteresis measurements were varied.



Figure 5.7. Experimental procedure for a single voltage hysteresis measurement

Voltage hysteresis measurements were conducted with four LiFePO₄ thin film samples. Sample LFP-H1 is 100 nm thick, LFP-H2 and LFP-H3 – 200 nm thick, LFP-H3L is the thin film from batch LFP-H3 coated with a 400 nm thick LiPON layer. The electrochemically active mass of the thin films were normalized based on their rate capabilities. Voltage hysteresis graphs and Butler – Volmer type dependence or overvoltage versus current are shown in Fig. 5.8.



Figure 5.8. Voltage hysteresis obtained at several currents for samples (a) LFP-H1,
(b) LFP-H2, (c) LFP-H3, (d) LFP-H3L; (e) Butler – Volmer type dependence between overvoltage and specific currents

The results indicate that, if 1–5% galvanostatic charge and discharge would be performed at intermediate SOC with infinitely low currents, there would be no voltage hysteresis or the observed voltage hysteresis would be extremely small. Even if voltage and current dependence at very small currents cannot be fitted with a linear line, there are still several data points indicating voltage hysteresis bellow 2 mV, which is at least an order of magnitude lower than reported in literature for LiFePO₄ bulk material [37].

The results contradict the expectations according to the current model, which predicts a non-vanishing voltage hysteresis due to non-monotonic lithium chemical potential – concentration dependence and sequential particle charging and discharging [37]. The disappearance of voltage hysteresis indicates that the sequential charging and discharging of LiFePO₄ particles in thin film can occur in a significantly different way than in bulk material. It is suspected that (de)lithiation could take place via a solid solution route, where instead of two phases (lithium-rich Li_{1-x}FePO₄ and lithium-poor Li_yFePO₄) only single phase Li_xFePO₄ is present with lithium distributed relatively homogenously throughout the thin film. This is feasible, since the grains in a thin film are tightly packed and they are not separated by a layer of carbon coating or electrolyte, and thus mass transfer between the grains can take place more efficiently. It must be noted that the voltage hysteresis measurements were performed within a relatively narrow state-of-charge range where on average amount of lithium corresponding to about 1% of the total capacity is removed and inserted in the LiFePO₄ thin film electrode.

Two more electrochemical phenomena have been observed for LiFePO₄ thin films. Firstly, at the first galvanostatic charging curve of a LiFePO₄ thin film an uncharacteristically high local electric potential maximum can be observed (see Fig. 5.9. (a)). Secondly, the memory effect has been observed in LiFePO₄ thin film, the results are shown in Fig. 5.9. (b), (c) and (d). The reader can learn more about the origins of the memory effect in the reference [37].

A precondition to being able to observe the memory effect (Fig. 5.9. (b), (c) and (d)) is the fact that a sequential particle-by-particle (de)lithiation takes place. The experimental procedure for memory effect measurements is shown in Fig. 5.10.



Figure 5.9. Electrochemical effects observed in LiFePO4 thin films: (a) a local maximum of the electric potential at the beginning of the charge (200 nA current), (b) and (c) memory effect with one and three write cycles and (d) potential difference due to the memory effect



Figure 5.10. The experimental procedure for memory effect measurements

The memory effect [37] is thought to arise when during a partial charge and discharge cycle only a part of the electrode is being (de)lithiated. After this partial charge and discharge cycle, some particles of the electrode are in a metastable state which leads to an increased electrode overpotential during a part of the next full charge or discharge. When comparing the results obtained for thin films with those seen for bulk material, the overpotential in the read cycle is more stretched out and not as localized as for bulk electrodes. This is likely explained by the different electrode of the thin film as compared to the bulk electrode.

Although slight voltage maximum has been observed for bulk materials before [37–41], it has never been as pronounced as in LiFePO₄ thin films obtained in this work (Fig. 5.9 a). We hypothesize that this is due to increased mechanical strain in the thin film when compared to the bulk material.

5.5. Electrophoretically deposited graphene and α -Fe₂O₃/TiO₂/GO anode for lithium ion batteries

Graphite is commonly used as an anode material for LIBs because of its high columbic efficiency, acceptable specific capacity and cyclic performance by forming intercalation compounds LiC_{6} [42]. However theoretical specific capacity of graphite is 372 mAh·g⁻¹ because of the limited Li-ion storage sites within the sp2 carbon structure [43]. One alternative to graphite has recently been reported - graphene nanosheets (GNS) obtained by various fabrication routes [7, 44]. Electrophoretic deposition (EPD) is an economical and versatile processing technique that has been applied for deposition of coatings and films. It has many advantages in the preparation of thin films from suspensions, such as high deposition rate and throughput, good uniformity and controlled thickness of the obtained films, no need of binders, and simplicity of scaling up [45]. Fabrication of graphene and CNT/graphene composite nanosheets by electrophoretic deposition technique was demonstrated before [45, 46]. However, the specific capacity values of graphene nanosheets obtained by EPD using a suspension in isopropanol have been dramatically reduced after the first discharge. In this study, the direct EPD method is used to prepare free standing porous graphene sheets from a suspension of graphene oxide (GO) in water, followed by a thermal reduction of as-deposited multilayers.

Among various transition metal oxides, hematite (α -Fe₂O₃) is among the most promising anode materials because of its non-toxicity, excellent stability and low cost [47, 48]. The incorporation of metal oxide nanoparticles will produce a porous network, and make excellent electron-conducting pathways. Hence, the nanostructured metal oxides loaded onto graphene can act as spacers to prevent the re-stacking of anode material layers during charge/discharge process. Therefore, graphene-metal oxide composites become an attractive issue to increase the cycling performance and rate capabilities of LIBs [48]. Among the transition metal oxides iron oxide, especially hematite (α -Fe₂O₃), is environmentally friendly and widely available, and an important industrial product. As the most stable iron oxide, α -Fe₂O₃ has been widely investigated in the fields of gas sensors, catalysis, energy storage, etc. [48, 49].

 TiO_2 has been studied for application in large-scale energy storage because it is a high-capacity and high-current rate tolerance material [8, 50, 51]. It has various nanostructure forms, such as nanorods, nanotubes, nanofibers and nano squares. However, low electronic conductivity and relatively low theoretical capacity (380 mAhg⁻¹) limit the applications of TiO₂. In addition, TiO₂ nanostructures collapse after electrochemical cycling, causing decreased charge capacity. The use of nanostructured TiO_2 -based materials may be an efficient approach to deal with the main problems of Li–ion batteries [50, 51].

Practical applications of TiO_2 in LIBs are limited by poor electrical conductivity and low chemical diffusivity of lithium – key factors for lithiation insertion in electrode materials. Therefore, it is highly desirable to develop new strategies for improve lithium kinetics in TiO_2 . There have been some research efforts in developing TiO_2 based nanomaterials for high performance energy conversion and storage devices [51]. Here, we report a novel α -Fe₂O₃/ TiO₂/graphene oxide composite anode prepared by electrophoretic deposition.

Fabrication of graphene sheet and metal oxide composite electrodes

Water suspension of graphene oxide was used for electrophoretic deposition of films under potentiostatic mode. GO was dispersed in de-ionized water at the concentration $10 \text{ mg} \cdot \text{mL}^{-1}$ and diluted to the concentration 1 mg·mL⁻¹ afterwards. Before the EPD process GO suspension was sonicated for 1 h in order to ensure homogenous dispersion. Electrodes used for EPD process were 1 mm thick 316 stainless steel substrates with a size of 1×4 cm. The distance between the two electrodes was 10 mm, and the applied electric field was 30 V·cm⁻¹ (DC power supply Agilent Technologies N5772A). Under the applied voltage, the negatively charged graphene oxide particles migrated toward the positive electrode and were subsequently orderly deposited on it. Thermal reduction of as-deposited GO films was performed by heating at 700 °C in argon/hydrogen flow (Ar: H₂ volume ratio – 95 : 5). The thickness of the graphene films was tuned ranging from several nanometers to a few micrometers by varying the deposition conditions, including the concentration of graphene oxide, the applied voltage, and the deposition time.

Composites of two metal oxides, α -Fe₂O₃ and anatase phase TiO₂ with a particle diameter 50 nm and 21 nm respectively (Sigma-Aldrich) were dissolved in 20 ml graphene oxide water suspension (BGT Materials, concentration 1mg/ml, flake size 1–20 µm). Electrophoretic deposition under potentiostatic mode was performed. Mass ratio of materials was 16.4 mg of α -Fe₂O₃ and 8.2 mg of TiO₂. Metal oxide powder before suspension was prepared and mixed in a ball mill (Retsch MM 200) for 20 minutes at 30 Hz. In order to obtain homogenous dispersion before EPD process, the suspension was sonicated one hour.

In order to apply electrodes within coin-type electrochemical cell thin film was electrophoretically deposited on a flat stainless steel discs (1 mm thick and 10 mm in diameter). Schematic illustration of electrode setup is presented in Fig. 5.11.



Figure 5.11. Structural model of electrode setup during anodic EPD and photographs of obtained thin films of different composites. (A)-FTGO, (B)-TGO, (C)-FGO

During deposition process, the negatively charged particles under the applied voltage migrate toward the positive electrode and subsequently deposit on it. Thermal reduction of as-deposited thin films was performed by heating for two hours at 580 °C in argon/ hydrogen flow (Ar : H_2 volume ratio was 95:5) [51]. Important parameters of as-prepared thin film are listed in Table 5.1.

Sample name	Composition	Ratio of mass, %	Thickness of film, μm	Weight of sample, mg
TGO	TiO ₂ /rGO	29/71	3 ± 0,2	$1.1 \pm 0,1$
FGO	Fe ₂ O ₃ /rGO	45/55	$2 \pm 0,2$	$1.7 \pm 0,1$
TFGO	TiO ₂ /Fe ₂ O ₃ /rGO	18/36/46	5 ± 0,2	$2.3 \pm 0,1$

Table 5.1. Parameters and preparation conditions of sample

Structure and morphology of graphene sheet and oxide composite electrodes

Results of XRD showed the presence of α -Fe₂O₃, rutile and anatase phases of TiO₂ (Fig. 5.12.). No detectable diffraction peaks from possible impurities are observed suggesting highly crystalline and purity of the as prepared films. The XRD patterns of samples are shown in Fig. 5.12. It is noteworthy to mention that the XRD pattern exhibits the typical diffraction peaks of few layer graphene (FLG) (002) at the peak position 26°. It means that most of the graphene oxide was successfully converted to rGO by thermal reduction and it has an interplanar distance of d = 0.34 nm calculated on the basis of Braggs equation [52].



Figure 5.12. XRD pattern and Raman spectra of TGO, FGO and FTGO composites (for interpretation of the references to color in this figure, reader is referred to the web version of this article)

Raman spectroscopy is an effective technique to detect the significant structural changes of graphene nanosheets based on the location and intensity of the relative peaks [53]. Raman spectroscopy was performed to indicate the structures of as-prepared thin films and structure of rGO by analyzing carbon D and G bands, see Fig. 5.12. The D band at 1350 cm⁻¹ is ascribed to defects and disordered carbon, while G band at 1580 cm⁻¹ arises from the zone centre E^{2g} mode, corresponding to ordered sp2 bonded carbon [53–57]. The Raman spectrum of all samples shows well referred documented D band peak due to the sp3 defects and another peak of G band corresponded to the inplane vibrations of sp2 carbon atoms and a doubly degenerated phonon mode at the Brillouin zone centre [56]. Raman spectra of obtained samples are plotted in Fig. 5.12. and shows relative intensities of D and G bands. It was observed that G band has a higher intensity than D band, it indicates an ordered sp2 bonded carbon and a successful reduction of GO to rGO.

It is clearly visible that the peak at 100 cm⁻¹ indicates the presence of α -Fe₂O₃ in both samples depicted in Fig. 5.12 (curves marked as red and blue). Two flat peaks (420 cm⁻¹ and 715 cm⁻¹) of TiO₂ sample indicate the presence of titanium dioxide [51].

The observed peaks of Raman shift for all the samples within Raman shift range of $0-1000 \text{ cm}^{-1}$ reveal the characteristic peaks of TiO₂ and α -Fe₂O₃. As can been seen, all curves contains a very broad reflection peak at the range of 2500–3500 cm⁻¹, indicating the presence of multilayered reduced graphene oxide. The change of 2D band peak intensity and location further proves that Fe₂O₃/TiO₂/rGO nanocomposites were successfully prepared. The second order of zone boundary phonons or 2D band, which is related to the stacking nature of graphene layers, was observed at 2700 cm⁻¹. The peak was broadened for the α -Fe₂O₃/TiO₂/rGO nanocomposite as a consequence of multilayer rGO sheets stacking caused by decrease of functional groups attached to the rGO, which prevents the sheets from restacking together. Raman analysis further confirmed that α -Fe₂O₃ and TiO₂ nanoparticles were effectively loaded among rGO sheets [55–57].

The morphology of graphene sheets obtained by EPD with the electric field $30 \text{ V}\cdot\text{cm}^{-1}$ was characterized by SEM, and their images are shown in Fig. 5.13. SEM images of graphene sheets exhibit a nanocrystalline structure with the particle size in the range of 200-400 nm. Such nanocrystalline structure has been obtained due to the water decomposition during the EPD process at a high voltage, followed by the intensive evolution of gases on the electrodes. Therefore, the obtained graphene films possess not only layered but also nanocrystalline structure, which is advantageous for enhanced Li-ion transport in films. SEM images of oxide composite layers in Fig. 5.13 (B, C) clearly depict the uniform wrapping of metal oxide particles by crinkled graphene sheets. As shown, the image indicates that TiO₂ and Fe₂O₃ nanoparticles were evenly anchored between the thin-layered rGO sheets (C). The layered graphene sheets accommodate the volume expansion of TiO₂ and Fe₂O₃ nanoparticles during the lithiation/delithiation process. The image (D) displays metal oxide grains intercalated by the flexible and ultrathin wrinkled rGO sheets with a few layers to form a sandwich structure.

Intercalation of metal oxide nanoparticles between graphene sheets plays a vital role to accumulate a large amount of lithium ion during charge/discharge process of the electrode. Furthermore, this unique morphology is beneficial to inhibit the aggregation of the graphene sheets [57, 58].



Figure 5.13. SEM images of thin films. (A) Fe₂O₃ nanograins with an average size of about 50 nm, (B, C) Fe₂O₃ and TiO₂ nanograins anchored on rGO layers, (D)-cross section of layered thin film structure

Electrochemical performance of electrodes from graphene sheets and oxide composites

Electrochemical properties of graphene sheets were first characterized by CV method. Typical cyclic voltammogram of GS electrode at 1 mV·s⁻¹ from 0.01 to 4 V vs. Li/Li⁺ is shown in Fig. 5.14 on the left. The CV profile is almost similar to the graphitic carbon with two cathodic and two anodic peaks [56, 57]. The wide reductive peak at around 1.2 V can be attributed to the formation of SEI film. The visible cathodic peak observed at around the potential 0.5 V and corresponding anodic peak at around 1.8 V complies to the Li-ion intercalation and deintercalation during the potential scan. This result is consistent with the charge-discharge voltage profiles (Fig. 5.14 on the right). The gravimetric charge capacity dependence on discharge current is shown in Fig. 5.15 on the right. At a slow discharge rate (I = 0.8 mA), gravimetric charge capacity of obtained GS anode reaches a high value ~ $1120 \text{ mAh} \cdot \text{g}^{-1}$ which is comparable or even higher than reported by other authors [44, 53, 54]. Increasing of discharge rate causes the gradual decrease of capacity. At much higher discharge rate (I = 2 mA), capacity falls to \sim 620 mAh·g⁻¹. The cycling behaviour of obtained GS electrodes at I = 2 mA within the voltage range of 0.01 to 4 V is shown in Fig. 5.15 on the left. It was found that after 50 cycles the reversible capacity of GS electrode still remains $\sim 530 \text{ mAh}\cdot\text{g}^{-1}$. The Coulombic efficiency for the first 50 cycles of GS electrode exceeded 85%. The further decrease of capacity during the cycling is negligible.



Figure 5.14. CV curve of graphene sheet electrode at the potential scan rate 1 mV·s-1 (left); galvanostatic charge-discharge profiles of graphene sheet electrode at the potential range 0.01-4 V (right)

Graphene sheets were fabricated by electrophoretic deposition method followed by thermal reduction. The results of scanning electron microscopy, X-ray diffraction and Raman spectroscopy confirm the formation of nanocrystalline graphene sheet films. The profile of voltammetric curves indicated smooth lithiation and delithiation processes of obtained graphene films. The initial discharge capacity was about 1120 mAh·g⁻¹ at a constant current density of 1 mA·cm⁻². Extended cycling was performed that demonstrated good reversibility of lithium intercalation and deintercalation in graphene sheet film with capacity retention over 85% after 50 cycles. The results show that nanocrystalline graphene sheets prepared by EPD exhibited a great potential for application as an anode material in lithium ion batteries because of the very nanocrystalline structure of GS, which promotes the Li-ion intercalation through the graphene layers. The use of lightweight graphene and lithium metal provides a high gravimetric capacity and energy density. The experimental results indicate that EPD is a highly powerful tool for the deposition of nanocrystalline graphene films from water suspension of graphene oxide.

The cycling performance of composite oxide samples is shown in Fig. 5.15 on the left. It was carried out in the voltage window of 0.01–3.8 V (vs. Li/Li⁺) at a constant discharge rate of 100 mA·g⁻¹ up to 150 cycles at ambient temperature (RT). The discharge capacity of FTGO is ~790 mAh·g⁻¹ that is higher than the capacity of TGO ~95 mAh·g⁻¹ and FGO ~240 mAh·g⁻¹. This can be attributed to the large electrochemical active surface of well-dispersed rGO and synergic effect of TiO₂ and α -Fe₂O₃ nanoparticles anchored on rGO and to the large area of SEI. Without the spacer of TiO₂ and α -Fe₂O₃ nanoparticles, rGO sheets easily stack together, therefore providing a small host area for lithium ions [58].

The initial capacity loss is 12% for FTGO, 21% for FGO, 15% for TGO after 150 cycles, and mainly resulted from diverse irreversible processes, such as interfacial lithium storage, inevitable formation of SEI layer, organic conductive polymer and electrolyte decomposition, which are common for most anode materials [36]. During cycling, it is clearly visible that after 40 cycles the capacity of TGO is decreased drastically, and then at the point when 140 cycles occurred, the capacity returns to the initial condition. For FGO electrode, the capacity slightly decreases within all the range of cycles. However, paradoxically, FTGO electrodes have shown a different electrochemical behaviour. At the first 50 cycles, the capacity slowly decreases and then begins to rise, finally even surpassing the initial value. This clearly demonstrates the improved reversibility of FTGO thin film electrode.



Figure 5.15. Reversible lithium storage capacities vs. cycle number (left) at a current density 100 mA·g⁻¹ (0.1 C) and CV curves (right) at a scan rate 4 mV·s⁻¹ of FGO, TGO and FTGO

The decay of reversible capacities of the FTGO during the first 50 cycles can be attributed to the pulverization of original TiO_2 and Fe_2O_3 *in situ* formed Fe and Ti nanoparticles during Li insertion and extraction process, which lead to the loss of electrical connectivity between neighbouring particles. In the initial cycles, the pulverized particles did not contact well with each other, as a result, the reversible capacity decreased. However, the Fe and Ti nanoparticles began to shrink and pulverize into small particles, when Li was extracted. With Li insertion and extraction, the formed Fe and Ti nanoparticles became smaller and smaller due to electrochemical milling effects and formed a strong attachment to the graphene sheets.

The excellent reversible capacities are also attributed to the critical size of Fe and Ti nanoparticles, where a smaller particle size can help to prevent the gradual aggregation into large clusters.

CV measurements were conducted to identify the electrochemical reactions occurred during lithiation/delithiation process of the TGO, FGO and FTGO hybrid films. Fig. 5.15 (right) shows three CV curves of the as-prepared electrodes at the scan rate of 4 mV·s⁻¹ within a cutoff voltage 0.005 and 4.0 V (vs. Li⁺/Li).

Charge storage behaviours of all samples were carried out, and a visible cathodic peak can be clearly observed at 1.5 V for FGO, 1.2 for TGO and 1.6 V for FTGO, and a corresponding anodic peak at 2.2 V for TGO, 2.6 V for FGO and 2.7 V for FTGO, respectively, which could be ascribed to the Li-ion intercalation and deintercalation during the potential scan. This result is consistent with the charge-discharge voltage profiles (Fig. 5.16).

Voltage versus capacity profiles as well as rate performance are illustrated in Fig. 5.16 A. The specific capacities and current densities of FGO, TGO and FTGO electrodes were figured out on the basis of the total weight α -Fe₂O₃, TiO₂ and rGO.

The increase of discharge rate causes the gradual decrease of gravimetric capacity. At the highest value of discharge rate (I = 500 mA), the capacity falls to ~42 mAh·g⁻¹ for TGO, ~65 mAh·g⁻¹ for FGO and ~390 mAh·g⁻¹ for FTGO, respectively. The first discharge (lithiation)/charge (delithiation) capacities of the electrodes at the current density of 0.05A/g and initial Coulombic efficiencies are listed in Table 5.2.



Figure 5.16. Galvanostatic charge-discharge profiles of (A) – TGO, (B) – FTGO, (C) – FGO composite electrodes at the potential range 0.03–3.6 V and discharge rate performance

	TGO/mAh·g ^{−1}	FGO/mAh·g ⁻¹	FTGO/mAh⋅g ⁻¹
Lithiation	95	240	790
Delithiation	40	190	520
CE/%	42	79	66
Theoretical capacities	661	879	765

Table 5.2. Gravimetric capacities and Coulombic efficiencies of samples

FTGO composite shows the best performance among three composites, and it may further prove the synergistic interaction between the rGO sheets, α -Fe₂O₃ and TiO₂ nanoparticles. The specific capacity was calculated by using complete mass of composite material.

However, the pure α -Fe₂O₃ and TiO₂ nanoparticles tend to agglomerate, hence providing a much smaller surface area for the transportation of lithium ions. Finally, the layered structure of reduced graphene facilitates the rapid Li-ion diffusion at both the electrode/electrolyte interface and within the bulk electrode, leading to enhanced electrochemical reaction kinetics and excellent cycle performance.

5.5. Summary

Both the cathode and anode materials for LIBs were developed during the project. Remarkable electrode improvements have been achieved by designing nanostructured materials, composites and thin films. The use of nanomaterials results in operating parameters close to their theoretical values and increases the charge capacity and cyclability of the Li-ion cells. The enhanced surface of nanomaterials also increases the charge transfer at the electrode – electrolyte interface. Additionally, lowering the particle size of active electrode material reduces the diffusion path of Li-ions and decreases the polarization of the electrodes. Nanostructured electrodes improve the structural stability and stabilize the solid electrolyte interface. Nanosized particles exhibit unique Li-ion storage mechanisms involving intercalation processes and/or conversion reactions.

Thin films of LiFePO₄ were obtained by PLD and magnetron sputtering techniques. The electrochemical performance of obtained cathode films was studied as a function of preparation technique, and the obtained electrode morphology, grain structure and composition. The discharge capacity of the thin films obtained by PLD reach 118 mAh·g⁻¹, which is slightly higher than that of the films obtained by magnetron sputtering (61 mAh·g⁻¹ at 0.1 C rate). However, the effective diffusion coefficients of PLD thin films (10⁻¹⁸ – 10⁻¹⁷ cm²/s) are lower than those of the films obtained by magnetron sputtering (10⁻¹⁴ – 10⁻¹² cm²/s), and besides the diffusion, they also generally characterize the overall lithium kinetics in the LiFePO₄ electrode. Voltage hysteresis was not observed for LiFePO₄ thin films deposited by PLD. The disappearance of voltage hysteresis indicates that the sequential charging and discharging of LiFePO₄ particles in thin film can occur in a significantly different way than in bulk material.

Reduced graphene oxide (rGO) sheets and composite thin films TiO₂/rGO, Fe₂O₃/rGO and TiO₂/Fe₂O₃/rGO obtained by electrophoretic deposition were studied as anode material for LIBs. Intercalation of metal oxide nanoparticles between reduced graphene oxide sheets plays a vital role to accumulate a large amount of lithium ion during charge/ discharge process of the electrode. Furthermore, this unique morphology is beneficial to inhibit the aggregation of the graphene sheets. At a slow discharge rate, the gravimetric charge capacity of obtained graphene sheet anode reaches a high value ~1120 mAh·g⁻¹, which is comparable to or even higher than that reported by other authors. The gravimetric charge capacity of α -Fe₂O₃/TiO₂/rGO films reaches 790 mAh·g⁻¹ that is much higher than the capacity of a single metal oxide composite with rGO, and exhibits excellent cyclability. The improved electrochemical properties were due to the rGO uniform dispersion in the inter-space of α -Fe₂O₃ and TiO₂, as well as the synergic effect between metal oxides and rGO.

5.6. References

- 1. Kucinskis, G., Bajars, G., and Kleperis, J. (2013) Graphene in lithium ion battery cathode materials: A review. *Journal of Power Sources*, 240, 66–79.
- 2. Ibrahim, H., Ilinca, A., and Perron, J. (2008) Energy storage systems characteristics and comparisons. *Renewable and Sustainable Energy Reviews*, 12(5), 1221–1250.
- 3. Whittingham, M. S. (2004) Lithium Batteries and Cathode Materials. *Chemical Reviews*, 104(10), 4271–4302.
- 4. Goodenough, J. B. (2007) Cathode materials: A personal perspective. *Journal of Power Sources*, 174(2), 996–1000.

- 5. Fergus, J. W. (2010) Recent developments in cathode materials for lithium ion batteries. *Journal of Power Sources*, 195(4), 939–954.
- Yang, Z., Ren, J., Zhang, Z., Chen, X., Guan, G., Qiu, L., et al. (2015) Recent Advancement of Nanostructured Carbon for Energy Applications. *Chemical Reviews*, 115(11), 5159–5223.
- 7. Kaprans, K., Bajars, G., Kucinskis, G., Dorondo, A., Mateuss, J., Gabrusenoks, J., et al. (2015) Electrophoretic Nanocrystalline Graphene Film Electrode for Lithium Ion Battery. *IOP Conference Series: Materials Science and Engineering*, 77(1), 012042.
- Kaprans, K., Mateuss, J., Dorondo, A., Bajars, G., Kucinskis, G., Lesnicenoks, P., et al. (2018) Electrophoretically deposited α-Fe₂O₃ and TiO₂ composite anchored on rGO with excellent cycle performance as anode for lithium ion batteries. *Solid State Ionics*, 319, 1–6.
- 9. Kucinskis, G. (2015) The study of nanostructured bulk and thin film LiFePO₄ cathode materials for lithium-ion batteries. Summary of Doctoral Thesis, University of Latvia, 2015.
- 10. Wasa, K., Kitabatake, M., and Adachi, H. (2004) Thin Film Materials Technology, Sputtering of Compound Materials. William Andrew, Inc.,
- 11. Ohring, M. (2002) Materials Science of Thin Films. Elsevier.
- Malik, R., Abdellahi, A., and Ceder, G. (2013) A Critical Review of the Li Insertion Mechanisms in LiFePO₄ Electrodes. *Journal of the Electrochemical Society*, 160(5), A3179–A3197.
- Tian, R., Liu, G., Liu, H., Zhang, L., Gu, X., Guo, Y., et al. (2015) Very high power and superior rate capability LiFePO₄ nanorods hydrothermally synthesized using tetraglycol as surfactant. *RSC Adv.*, 5(3), 1859–1866.
- Lung-Hao Hu, B., Wu, F.-Y., Lin, C.-T., Khlobystov, A.N., and Li, L.-J. (2013) Graphenemodified LiFePO₄ cathode for lithium ion battery beyond theoretical capacity. *Nature Communications*, 4, 1687.
- 15. Wang, J. and Sun, X. (2015) Olivine LiFePO₄: the remaining challenges for future energy storage. *Energy Environ. Sci.*, 8(4), 1110–1138.
- 16. Zaghib, K., Guerfi, A., Hovington, P., Vijh, A., Trudeau, M., Mauger, A., et al. (2013) Review and analysis of nanostructured olivine-based lithium recheargeable batteries: Status and trends. *Journal of Power Sources*, 232, 357–369.
- 17. McCready, D. E., Liang, Y., Shutthanandan, V., Wang, C. M., and Thevuthasan, S. (2006) Thermal Lattice Expansion in Epitaxial SrTiO3(100) on Si(100), *Advances in X-Ray Analysis*, ISSN 1097, 175–179.
- 18. de Ligny, D. and Richet, P. (1996) High-temperature heat capacity and thermal expansion of SrTiO₃ and SrZrO₃ perovskites. *Physical Review B.*, 53(6), 3013–3022.
- 19. Chen, Z., Ren, Y., Qin, Y., Wu, H., Ma, S., Ren, J., et al. (2011) Solid state synthesis of LiFePO₄ studied by in situ high energy X-ray diffraction, *Journal of Materials Chemistry*, 21, 5604.
- 20. Tang, K., Yu, X., Sun, J., Li, H., and Huang, X. (2011) Kinetic analysis on LiFePO₄ thin films by CV, GITT, and EIS. *Electrochimica Acta.*, 56(13), 4869–4875.
- Palomares, V., Ruiz de Larramendi, I., Alonso, J., Bengoechea, M., Goñi, a., Miguel, O., et al. (2010) LiFePO₄ thin films grown by pulsed laser deposition: Effect of the substrate on the film structure and morphology. *Applied Surface Science*, 256(8), 2563–2568.
- 22. Köhler, M., Berkemeier, F., Gallasch, T., and Schmitz, G. (2013) Lithium diffusion in sputterdeposited lithium iron phosphate thin-films. *Journal of Power Sources*, 236, 61–67.
- Chiu, K.-F. (2007) Optimization of Synthesis Process for Carbon-Mixed LiFePO₄ Composite Thin-Film Cathodes Deposited by Bias Sputtering. *Journal of the Electrochemical Society*, 154(2), A129.
- Hong, J., Wang, C., Dudney, N. J., and Lance, M. J. (2007), Characterization and Performance of LiFePO₄ Thin-Film Cathodes Prepared with Radio-Frequency Magnetron-Sputter Deposition. *Journal of The Electrochemical Society*, 154(8), A805.
- Xie, J., Imanishi, N., Zhang, T., Hirano, A., Takeda, Y., and Yamamoto, O. (2009) Li-ion diffusion kinetics in LiFePO₄ thin film prepared by radio frequency magnetron sputtering. *Electrochimica Acta*, 54(20), 4631–4637.
- 26. Zhu, X.-J., Cheng, L.-B., Wang, C.-G., Guo, Z.-P., Zhang, P., Du, G.-D., et al. (2009) Preparation and Characteristics of LiFePO₄ Thin Film by Radio Frequency Magnetron

Sputtering for Lithium Microbatteries. The Journal of Physical Chemistry C., 113(32), 14518-14522.

- 27. Lu, Z. G., Lo, M. F., and Chung, C. Y. (2008) Pulse Laser Deposition and Electrochemical Characterization of LiFePO₄ C Composite Thin Films. *J. Phys. Chem. C*, 112,7069–7078.
- 28. Sauvage, F., Baudrin, E., Gengembre, L., and Tarascon, J. (2005) Effect of texture on the electrochemical properties of LiFePO₄ thin films. *Solid State Ionics*, 176(23-24), 1869–1876.
- 29. Yada, C., Iriyama, Y., Jeong, S.-K., Abe, T., Inaba, M., and Ogumi, Z. (2005) Electrochemical properties of LiFePO₄ thin films prepared by pulsed laser deposition. *Journal of Power Sources*, 146(1-2), 559–564.
- 30. Song, S.-W., Reade, R. P., Kostecki, R., and Striebel, K. A. (2006) Electrochemical Studies of the LiFePO₄ Thin Films Prepared with Pulsed Laser Deposition. *Journal of The Electrochemical Society*, 153(1), A12.
- 31. Zhu, C., Weichert, K., and Maier, J. (2011) Electronic Conductivity and Defect Chemistry of Heterosite FePO₄. *Advanced Functional Materials*, 21(10), 1917–1921.
- 32. Li, Y., El Gabaly, F., Ferguson, T. R., Smith, R. B., Bartelt, N. C., Sugar, J. D., et al. (2014) Current-induced transition from particle-by-particle to concurrent intercalation in phaseseparating battery electrodes. *Nature Materials*, 13(12), 1149–1156.
- Zhu, Y. and Wang, C. (2010) Galvanostatic Intermittent Titration Technique for Phase-Transformation Electrodes. *The Journal of Physical Chemistry C.*, 114(6), 2830–2841.
- 34. Prosini, P. P., Lisi, M., Zane, D., and Pasquali, M. (2002) Determination of the chemical diffusion coefficient of lithium in LiFePO₄. *Solid State Ionics*, 148(1–2), 45–51.
- Churikov, A. V., Ivanishchev, A. V., Ivanishcheva, I. A., Sycheva, V. O., Khasanova, N. R., and Antipov, E. V. (2010) Determination of lithium diffusion coefficient in LiFePO4 electrode by galvanostatic and potentiostatic intermittent titration techniques. *Electrochimica Acta*, 55(8), 2939–2950.
- Bajars, G., Kucinskis, G., Smits, J., Kleperis, J., and Lusis, A. (2012) Characterization of LiFePO4 /C Composite Thin Films Using Electrochemical Impedance Spectroscopy. *IOP Conference Series: Materials Science and Engineering*, 38(1), 012019.
- 37. Sasaki, T., Ukyo, Y., and Novák, P. (2013) Memory effect in a lithium-ion battery. *Nature Materials*, 12(6), 569-575.
- Kang, B. and Ceder, G. (2009) Battery materials for ultrafast charging and discharging. *Nature*, 458(7235), 190-3.
- Shang, W., Kong, L., and Ji, X. (2014) Synthesis, characterization and electrochemical performances of LiFePO₄/graphene cathode material for high power lithium-ion batteries. *Solid State Sciences*, 38, 79–84.
- Li, J., Wu, J., Wang, Y., Liu, G., Chen, C., and Liu, H. (2014) Synthesis of LiFePO₄/C composite with high rate capability using spheniscidite as a facile precursor. *Materials Letters*, 136, 282–285.
- Kim, K.M., Lee, Y.-G., Kang, K.-Y., Yang, Y.S., and Kim, J. (2012) A simple method for solving the voltage overshoots of LiFePO₄-based lithium-ion batteries with different capacity classes. *RSC Advances*, 2(9), 3844.
- Goriparti, S., Miele, E., De Angelis, F., Di Fabrizio, E., Proietti Zaccaria, R., and Capiglia, C. (2014) Review on recent progress of nanostructured anode materials for Li-ion batteries. *Journal of Power Sources*, 257, 421–443.
- 43. Nitta, N., Wu, F., Lee, J.T., and Yushin, G. (2015) Li-ion battery materials: present and future. *Materials Today*, 18(5), 252–264.
- 44. Dao, T.D., Hong, J.-E., Ryu, K.-S., and Jeong, H.M. (2014) Super-tough functionalized graphene paper as a high-capacity anode for lithium ion batteries. *Chemical Engineering Journal*, 250, 257–266.
- Wu, Z.-S., Pei, S., Ren, W., Tang, D., Gao, L., Liu, B., et al. (2009) Field Emission of Single-Layer Graphene Films Prepared by Electrophoretic Deposition. *Advanced Materials*, 21(17), 1756–1760.

- 46. Seo, S.-D., Hwang, I.-S., Lee, S.-H., Shim, H.-W., and Kim, D.-W. (2012) 1D/2D carbon nanotube/graphene nanosheet composite anodes fabricated using electrophoretic assembly. *Ceramics International*, 38(4), 3017–3021.
- Chen, D., Ji, G., Ma, Y., Lee, J.Y., and Lu, J. (2011) Graphene-Encapsulated Hollow Fe₃O₄ Nanoparticle Aggregates As a High-Performance Anode Material for Lithium Ion Batteries. ACS Applied Materials & Interfaces, 3(8), 3078–3083.
- 48. Yan, Y., Tang, H., Li, J., Wu, F., Wu, T., Wang, R., et al. (2017) Self-assembly synthesis of a unique stable cocoon-like hematite @C nanoparticle and its application in lithium ion batteries. *Journal of Colloid and Interface Science*, 495, 157–167.
- 49. Wu, Z.-S., Zhou, G., Yin, L.-C., Ren, W., Li, F., and Cheng, H.-M. (2012) Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy*, 1(1), 107–131.
- Yu, Y., Sun, D., Wang, H., and Wang, H. (2016) Electrochemical Properties of Rutile TiO₂ Nanorod Array in Lithium Hydroxide Solution. *Nanoscale Research Letters*, 11(1), 448.
- 51. Wen, Z., Ci, S., Mao, S., Cui, S., He, Z., and Chen, J. (2013) CNT@TiO₂ nanohybrids for high-performance anode of lithium-ion batteries. *Nanoscale Research Letters*, 8(1), 499.
- 52. Van Meveren, M. M. (2017) Graphene-Based "Hybrids" as High-Performance Electrodes with Tailored Interfaces for Alternative Energy Applications: Synthesis, Structure and Electrochemical Properties. Western Kentucky University, 2017.
- 53. Bai, L.-Z., Zhao, D.-L., Zhang, T.-M., Xie, W.-G., Zhang, J.-M., and Shen, Z.-M. (2013) A comparative study of electrochemical performance of graphene sheets, expanded graphite and natural graphite as anode materials for lithium-ion batteries. *Electrochimica Acta*, 107, 555–561.
- 54. Guo, P., Song, H., and Chen, X. (2009) Electrochemical performance of graphene nanosheets as anode material for lithium-ion batteries. *Electrochemistry Communications*, 11(6), 1320–1324.
- 55. Wu, Q.-H., Qu, B., Tang, J., Wang, C., Wang, D., Li, Y., et al. (2015) An Alumina-Coated Fe₃O₄-Reduced Graphene Oxide Composite Electrode as a Stable Anode for Lithium-ion Battery. *Electrochimica Acta*, 156, 147–153.
- Zhou, X., Zhang, J., Su, Q., Shi, J., Liu, Y., and Du, G. (2014) Nanoleaf-on-sheet CuO/graphene composites: Microwave-assisted assemble and excellent electrochemical performances for lithium ion batteries. *Electrochimica Acta*, 125, 615–621.
- 57. Wang, D., Choi, D., Li, J., Yang, Z., Nie, Z., Kou, R., et al. (2009) Self-Assembled TiO₂-Graphene Hybrid Nanostructures for Enhanced Li-Ion Insertion. *ACS Nano*, 3(4), 907–914.
- Wei, D., Liang, J., Zhu, Y., Zhang, J., Li, X., Zhang, K., et al. (2013) Facile formation of graphene-encapsulated α-Fe₂O₃ nanorice as enhanced anode materials for lithium storage. *Electrochimica Acta*, 114, 779–784.

5.7. Kopsavilkums

Projekta laikā tika izstrādāti jauni katoda un anoda materiāli litija jonu baterijām ar uzlabotām elektroķīmiskajām īpašībām, kas tika panāktas, veidojot nanostrukturētus materiālus, kompozītmateriālus un plānās kārtiņas. Nanomateriālu izmantošana dod iespēju sasniegt darbības parametrus, kas ir tuvi to teorētiskajām vērtībām un palielina litija jonu elektroķīmisko šūnu lādiņietilpību un ciklējamību. Nanomateriālu palielinātā aktīvā virsma samazina arī lādiņu pārneses pretestību caur elektroda-elektrolīta robežvirsmu. Turklāt elektrodu materiāla daļiņu izmēra samazināšana saīsina litija jonu difūzijas ceļu un samazina elektrodu polarizāciju. Nanostrukturētie elektrodi uzlabo arī struktūras stabilitāti un stabilizē elektroda robežvirsmu ar cieto elektrolītu. Nanoizmēru daļiņas uzrāda arī unikālus litija jonu uzkrāšanas mehānismus, kas ietver interkalācijas procesus un/vai konversijas reakcijas.

Plānās LiFePO₄ kārtiņas tika iegūtas, izmantojot impulsa lāzera nogulsnēšanas (PLD) un magnetrona izputināšanas metodi. Iegūto katodmateriālu kārtiņu elektroķīmiskās īpašības tika pētītas atkarībā no to iegūšanas metodes, elektrodu morfoloģijas, graudu struktūras un sastāva. PLD plāno kārtiņu lādiņietilpība sasniedz 118 mAh·g⁻¹, kas ir nedaudz lielāka nekā kārtiņām, kuras iegūtas magnetrona izputināšanas rezultātā (61 mAh·g⁻¹ pie 0.1 C uzlādes/izlādes ātruma). Tomēr PLD plāno kārtiņu efektīvie difūzijas koeficienti (10⁻¹⁸–10⁻¹⁷ cm²/s) ir zemāki nekā ar magnetrona izputināšanas metodi iegūtajām kārtiņām (10⁻¹⁴–10⁻¹² cm²/s), un vairumā gadījumu tie raksturo ne tikai difūzijas procesus, bet arī kopējo litija kinētiku LiFePO₄ elektrodā. Ar PLD metodi iegūtajās LiFePO₄ plānajās kārtiņās netika novērota sprieguma histerēze. Sprieguma histerēzes trūkums liecina, ka LiFePO₄ daļiņu uzlāde un izlāde plānās kārtiņas gadījumā var notikt ievērojami atšķirīgā veidā nekā pulverveida materiālā.

Vairākslāņu reducētā grafēna oksīda (rGO) un kompozītu TiO₂/rGO, Fe₂O₃/rGO un TiO₂/Fe₂O₃/rGO plānās kārtiņas, kas iegūtas ar elektroforētiskās nogulsnēšanas metodi, tika pētītas kā anoda materiāls litija jonu baterijām. Metāla oksīdu nanodaļiņu interkalācijai starp reducētā grafēna oksīda slāņiem ir svarīga loma, lai akumulētu lielu daudzumu litija jonu elektroda uzlādes/izlādes procesā. Turklāt šī unikālā morfoloģija kavē rGO slāņu agregāciju. Vairākslāņu rGO anoda gravimetriskā lādiņietilpība, kas iegūta pie maza izlādes ātruma, sasniedz augstu vērtību ~1120 mAh·g⁻¹ un ir salīdzināma vai pat augstāka, nekā ziņots citu autoru pētījumos. α -Fe₂O₃/TiO₂/rGO gravimetriskā lādiņietilpība sasniedz 790 mAh·g⁻¹, kas ir daudz lielāka nekā viena atsevišķa metāla oksīda kompozīta ar rGO lādiņietilpība. Turklāt tas uzrāda izcilu ciklējamību. Uzlabotās elektroķīmiskās īpašības ir saistītas ar rGO viendabīgu dispersiju tilpumā starp α -Fe₂O3 un TiO₂, kā arī sinerģisku efektu starp metāla oksīdiem un rGO.