

Recent studies on germanium-nanomaterials for LIBs anodes

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Abstract. The inherently low capacity of the classically used carbon-based anode is one of the major drawbacks hindering the wide application of lithium ion batteries (LIBs) in electric vehicles. Carbon replacement with materials possessing high theoretical capacity, such as germanium (Ge) represents one of the approaches used for ensuring wider LIBs’ implementation. The main disadvantage of the Ge use is its huge volume change during the lithiation / delithiation, causing Ge-based electrodes pulverization, deterioration of the electrochemical properties and resulting in electrodes relatively short life. Usage of Ge based nanomaterials is regarded as powerful tool for overcoming the mentioned drawbacks. This paper reviews and discusses the very recent progress in the preparation and studying the Ge nanoparticles (NPs), Ge nanoalloys and Ge-based nanocomposites as attempts for preparation of advanced anodes for LIBs.

1 Introduction

The lithium-ion batteries are widely used and their application in portable electronics and electric vehicles or hybrid electric vehicles is expected to be increased. LIBs are rechargeable batteries possessing high energy density, low self-discharge and no memory effect. Every LIB (more correctly a battery pack) consists of gathered together electrically connected electrochemical cells and electronics for control and protection. The cell (that is the primary electrochemical unit) contains electrodes, separator, and electrolyte. In the most commercial cells the negative electrode (anode) is made of graphite.

The positive electrode is a lithium-based material. It can be a layered oxide (for example lithium cobalt oxide), a polyanion (like lithium iron phosphate), or a spinel (for instance lithium manganese oxide). The electrolyte usually represents a mixture of organic carbonates, typically ethylene carbonate (EC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), containing lithium complexes, such as lithium hexafluorophosphate (LiPF₆), lithium perchlorate (LiClO₄), lithium tetrafluoroborate (LiBF₄), lithium hexafluoroarsenate monohydrate (LiAsF₆), and lithium triflate (LiCF₃SO₃).

Anode and cathode allow lithium ions (Li⁺) to move in and out of their framework, the Li⁺ insertion process (lithiation) is called intercalation and the Li⁺ extraction (delithiation) one – deintercalation. During the discharge an oxidation reaction proceeds at the anode and positively charged Li⁺ and negatively charged electrons are formed. The Li⁺ move through the electrolyte to the cathode where they are inserted in the cathode material (often forming a lithium compound) with the aid of

electrons that are transported from anode through an external circuit to the cathode. When the cell is being charged, the reverse reaction occurs – the Li⁺ and electrons move back into the negative electrode.

The capacity decrease in LIBs is most often due to the loss of lithium to the solid-electrolyte interphase (SEI) that forms at the negative electrode. Initially, during charging at temperature below 25 °C metallic lithium is produced spontaneously on the electrode surface. Further the lithium reacts with electrolyte to form Li₂O, LiF, Li₂CO₃, and polyolefins. This is due to the fact that the electrolytes typically used in LIBs are not stable at the electrode operating potential during charging and they may decompose. At the beginning, SEI formation increases the electrode resistance to solvent decomposition but the increase in the SEI thickness with time leads to a gradual decrease of the LIB’s capacity.

The commercial graphite exhibits a relatively low theoretical capacity of 372 mAh/g (electrode capacities are compared by using three measures: specific energy or gravimetric capacity (capacity per unit of mass), volumetric capacity (capacity per unit volume), and areal capacity (area-normalized specific capacity)). This fact leads to an intensive search for other materials. Materials forming alloys with Li, such as Si, Ge, Sn are actively researched as alternatives to carbon-based anodes for rechargeable LIBs due to their higher theoretical capacities in comparison to commercial graphite. For example, Ge possesses theoretical specific capacity of 1600 mAh/g (at 4.4 Li⁺ per Ge atom), an electronic conductivity 10⁴ times higher than silicon, and high Li⁺ diffusivity (more than 400 times higher than that in silicon at room temperature) [1].

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The unsatisfying cycle life (due to the volume expansion / contraction during the lithiation / delithiation reaction, causing the formation of cracks, pulverization of the electrodes, destroying the conductive network of the electrode, thus deteriorating the storage capacity of lithium and worsening the cycle performance) appeared as one of the most challenging problems of the recently developed anode materials. Ge particles aggregation during the Li^+ insertion / extraction leads to an increase in the internal resistance and in Li^+ diffusion path resulting in inability of the internal Ge particles to participate in chemical reactions. The final result is capacity loss and more generally – poor electrochemical performance.

The investigations trying to solve the above-mentioned problems are going to the following directions: (a) alloying with the Li-active / inactive materials, (b) preparing nano-structured electrodes, and (c) surface modification by introducing conducting and / or nonconducting buffer components [2].

Application of nanostructured materials is considered a promising approach for bettering the electrochemical properties of electrodes. Nanostructured electrodes possess a very large specific surface area that can increase the contact area between the electrodes and the electrolyte. This big contact area is able to accelerate the exchange of ions and electrons at the electrode / electrolyte interface. Furthermore, owing to their very short internal diffusion paths, the nanoscale materials possess much higher ionic or electronic conductivities compared to their bulk counterparts. In addition, they can also resist to bigger mechanical deformation during charge / discharge cycling. Since Ge possesses high theoretical capacity, good electrical conductivity and fast Li^+ diffusivity, Ge-based nanomaterials have recently attracted considerable attention as LIB electrode materials.

Recently, different nanoscale Ge-based anodes with a variety of morphologies have been developed to raise the electrochemical performances of these anodes and the results are presented in the worldwide literature.

The most comprehensive overview of anodes for LIBs is provided by Hu and co-authors [3]. The paper covers studies carried out till the first quarter of 2016. The paper has extensively reviewed the preparation and the entire characterization of nanoparticles (NPs), nanowires (NWs), and nanotubes (NTs) made of single Ge, Ge alloys with metals (such as Cu, Sn), with semiconductors (such Si, Se), and germanium chalcogens alloys such as GeS.

Preparation of electrodes based on Ge/carbon nanotubes (CNTs), Ge/graphene, Ge-reduced graphene oxide-CNTs (Ge-RGO-CNTs), Ge-reduced graphene oxide nanofibres (Ge@RGO NFs) aimed at achieving a longer cycling life of the LIBs and their characterization is also presented by the same paper.

A special attention is paid to the preparation and characterization of core-shell structural electrodes because of their high conductivity, excellent stability and the ability to prevent the significant volume changes in the Ge electrode during the charge/discharge process. LIB anodes based on Ge@C core-shell; Ge@Cu core-shell; Ge@C/graphene, Ge@C/RGO, Cu@Ge core-shell

NW; and 3D TiO_2 @Ge core-shell nanorod arrays on carbon textiles are briefly discussed.

Attention is drawn also to LIB anodes made of Ge based nanomaterials (NWs, NPs, and nanorods) that are ternary alloys and their composites (such as $\text{Cu}_3\text{Ge}/\text{Ge}$ NWs, $\text{Cu}_3\text{Ge}/\text{Ge}@$ graphene aerogel), as well as double oxides and their composites (such as CuGeO_3 , $\text{Cu}_3\text{Ge}/\text{GeO}_x/\text{CuGeO}_3$ NWs, CuGeO_3 NWs / graphene composites, $\text{CuGeO}_3@$ RGO composites, $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ NWs on carbon textiles, $\text{Ca}_2\text{Ge}_7\text{O}_{16}$ NW/ graphene sheet nanocomposite, Zn_2GeO_4 NWs and nanorods, Zn_2GeO_4 -GO nanocomposite, Cd_2GeO_4 NWs, Cd_2GeO_4 NW / CNT and the Cd_2GeO_4 NW/GO/CNT nanocomposite films, PbGeO_3 NWs, SrGe_4O_9 and BaGe_4O_9 NWs).

The results from testing the all above-mentioned materials as anodes in cells for LIBs are also presented.

Additionally, a brief discussion is given on the performance of LIBs electrodes made of germanium oxide (GeO_2) NPs, GeO_2 NPs/RGO composite, and GeO_2 -C fibre composite.

Influence of the LIB's electrolyte type, the discharge current density, the working temperature, the cycling rate¹, the shape and morphology of the Ge-based materials has been presented when it was discussed in the original papers.

For all presented electrodes data are provided on the specific capacity (mAh/g) – initial and after cycling, current density (mA/g) and the number of charge-discharge cycles. However, for comparative purposes, the data presented have to be used cautiously, going to the original papers to check the exact cycling rate and the number of cycles related to the reported specific capacities and current densities.

An other review paper is devoted to the advances in studies on the synthesis, optical properties and applications of germanium nanocrystals, including their use as anodes for LIBs [4]. The paper covers studies carried out in the period 2010-2015 and only two of the papers reviewed in [3] are referred to also in [4]. The author pays special attention to the Ge nanocrystals (NCs) use in anodes for LIBs. The Ge NCs/RGO composite and a composite of Ge NCs encapsulated within carbon nanofibers ((Ge)0D@(CNF)1D) are presented, including means for those composites preparation, their characterization and results from their testing as anodes for LIBs (specific capacity (mAh/g) – initial and after cycling at different rate, and the number of charge-discharge cycles).

Figure 1 presents schematically the major Ge-based nanomaterials studied until 2016 as potential anode (active) materials for LIBs.

Having in mind the importance of developing high-performance LIBs and the exponentially growing studies in the area, we consider that it would be useful for the

¹ A C-rate is a standard unit of the rate at which a battery is discharged with respect to its maximum capacity. A 1C rate denotes that the discharge current will discharge the whole battery in 1 hour. As an example, for a battery with a capacity of 100 Ah, 1C is equal to a discharge current of 100 A, a 5C rate for this battery would be 500 A. (http://web.mit.edu/evt/summary_battery_specifications.pdf)

reader to be supplied with up-to-dated information on the subject.

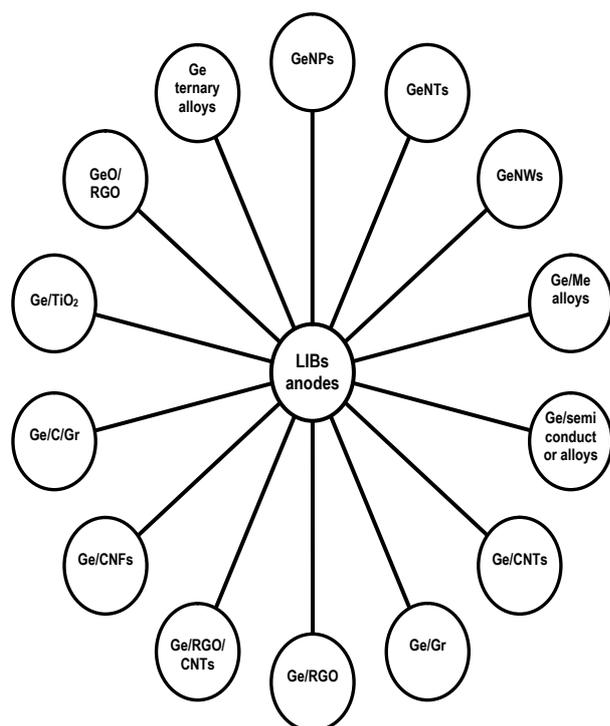


Fig. 1. Schematic representation of the major Ge-based nanomaterials studied until 2016 as potential anode (active) materials for LIBs

In this mini-review article, we overview the further development in the use of Ge-based nanomaterials and nanocomposites for LIBs' anodes by covering the studies in the recent three years.

2 Recent approaches for preparing germanium based nanomaterials for high-performance anodes for LIBs

The studies aimed at improving the performance of Ge containing LIBs anodes in the recent 3-4 years have continued in the following directions: nano-structured germanium, germanium oxide based materials, germanium alloys based nanomaterials and preparation of electrodes based on Ge and carbon (or its derivatives).

2.1 Nano-structured germanium

A new direction in the synthesis Ge-based nanomaterials for LIBs is proposed that relies on pulsed laser-assisted electrodeposition from ionic liquid at room temperature [5]. The utilized ionic liquid was 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([EMIm]Tf₂N) that did not require supporting electrolytes as is the case with organic solvents. The laser irradiation allowed for controlling the size, shape, and distribution of nanoparticles since it ensured clustering and vertical growth of Ga nanospheres and further development of Ge nanowires (non-branched and

branched). The pulsed laser irradiation facilitated the direct electrodeposition of Ge nanowires on a copper (Cu) foil.

The characteristics of the produced material were studied utilizing home-made cells. The Ge NW electrode was used to prepare coin-type half cells (2025R size) by applying Li metal as the counter electrode. The separator was a microporous polyethylene (PE) and the electrolyte was 1 mol/L LiPF₆ in EC-DEC mixture. The prepared Ge nanowire anode exhibited an initial discharge capacity of 1646 mAh/g and initial charge capacity of 1278 mAh/g. The large initial discharge capacity and irreversible capacity loss measured were assigned to the irreversible formation of SEI. However, the capacity reversibility was much better in the next cycles and the capacity of 884 mAh/g was retained after 50 cycles at 0.2C, while the coulombic efficiency (CE) was higher than 96%. The capacity decay was less pronounced compared to that observed for Ge nanoparticle film prepared by non laser-assisted electrodeposition.

The studied Ge nanowire electrode showed reversible capacities of 1230, 1160, 1070, 960, and 730 mAh/g at 0.1C, 0.2C, 0.5C, 1C, and 2C, correspondingly. In addition, the capacity returned to 1100 mAh/g when the rate was decreased to 0.1C. These findings show that the properties of pure Ge anodes can be improved by pulsed laser assisted ionic liquid electrodeposition. The improved properties of thus prepared electrode were assigned to the laser-assisted transformation of the amorphous Ge deposits from films in the absence of laser irradiation to polycrystalline structures (nanowires and branched nanowires) under laser irradiation. This structure supplies channels facilitating the transport of Li⁺. The result is higher diffusion rate of Li⁺. The polycrystallinity of the nanostructures also averts pulverization of the electrode materials during LIBs' cycling by facilitating volumetric expansion throughout the entire nanostructure.

Preparation of porous structures is considered an efficient way for mitigating the negative effect of the LIBs' volume expansion and contraction during lithiation and delithiation. In this line, a 3D ordered macroporous (3DOM) nickel (Ni) framework (Ge/3DOM-Ni) was prepared by using drop-coating technique to attach Ge nanoparticles to the Ni framework [6]. Germanium nanoparticles were produced by reduction of germanate ions with NaBH₄, the former were prepared through reaction of GeO₂ with NaOH. Thus prepared Ge nanoparticles were dispersed in ethanol by ultrasonication. The obtained suspension was drop-coated onto the heated 3DOM-Ni framework. The self-supporting porous Ge/3DOM-Ni electrodes were produced by annealing the 3DOM-Ni framework, bearing the Ge nanoparticles, at 500 °C for 2 h in Ar atmosphere.

To study the properties of thus prepared anodes a coin-type half cells (2025R size) were assembled. Microporous PE was used as the separator, Li metal as counter and reference electrode, and 1M LiPF₆ in EC – DEC (1:1 vol.%) as the electrolyte. The discharge-charge study was carried out at a current density of 0.2C (1C is approximately 1600 mA/g) within the potential range of 0.01–2 V (vs. Li⁺/Li). Initially a low CE of

53.3% was recorded, corresponding to the initial discharge and charge capacities of approximately 1869 and 996 mAh/g. This effect is assigned to the SEI layer formation. The discharge and charge capacities for the second cycle were 1053 and 1052 mAh/g, correspondingly, ensuring the CE of approximately 100%. No definite variation was observed in the specific charge capacities of the Ge/3DOM-Ni electrodes in the initial 10 cycles, pointing at good structural stability. After 100 cycles a specific charge capacity of 610 mAh/g was observed while the CE remained c.a. 100%.

The rate performance of the Ge/3DOM-Ni electrode was studied at rates of 0.1C, 0.2C, 0.5C, 1C, 2C, 5C, and 10C. The obtained respective reversible capacities of the Ge/3DOM-Ni electrodes were approximately 1337, 1042.5, 930, 817.5, 685, 460, and 270 mAh/g. The good performance of the Ge/3DOM-Ni electrode is mainly attributed to the 3DOM-Ni framework, since the easily accessible macroporous channels ensure efficient transport pathways for electrolyte and Li^+ and highly conductive framework for electron transport. The high porosity of the prepared electrode (confirmed by SEM observations) helped to avoid the negative effect of the volume enlargement of the Ge nanoparticles at cycling. The work showed that porous Ni frameworks are good supports and current collectors for Ge-based LIBs anodes. The use of polymer binders and conductive substances is avoided, thus the specific capacity is increased.

Recently a study is reported on the effect of mass loading on the areal capacity, capacity retention, and rate performance in high-capacity Ge electrodes for LIBs [7]. The results are of interest, since the application of electrodes with an areal capacity over 3 mAh/cm² meets different obstacles, such as electrode delamination from the current collector, increased resistance – electronic and ionic, substandard electrolyte penetration, and underutilization of the electrode at high current densities. To overcome the problems, a porous Ge was prepared by reducing GeO_2 under hydrogen atmosphere at 450 °C. Further the slurry was prepared by mixing 70 wt.% of the produced active material with the binder (20 wt.% poly (acrylic acid) and the conductive agent (10 wt.% acetylene black). The electrodes were elaborated by tape casting of the produced slurry.

To study the electrochemical behaviour of the prepared electrodes CR2016 coins cells were fabricated. Metal Li was used as the counter electrode for the half cells and commercial LiCoO_2 electrodes were applied in studies on the full cell cyclic performance. The electrolyte applied consisted of 1M LiPF_6 in mixture of ED, DEC and DMC (1:1:1 by volume).

The electrochemical behaviour of the Ge electrode was studied using galvanostatic charge/discharge process in the range of 0.02 and 1.2 V vs Li/Li^+ . At a current density of 1000 mA/g, 340 stable cycles were achieved and the final specific capacity was approximately 1300 mAh/g for the mass loading of c.a. 1 mg/cm². The slight capacity drop in the initial cycles was assigned to the formation of SEI, as well as to some loss of electrical contact due to the rearrangement of active materials. The increase in the specific capacity at further cycling is

assigned to the electrode activation by the deeper lithiation into the active materials. The first cycle CE was 60%, it increased to 92% for the 2nd cycle, and reached approximately 99% for the 10th cycle.

The electrode cyclic performance was studied (up to 1800 cycles) at the high current density of 5C (i.e. 8 A/g, since 1C = 1600 mA/g) and at the low loading of 0.56 mg/cm². A CE over 99% was achieved starting from the 3rd cycle. This long term cycleability at the high rate was explained by the porous morphology of the Ge electrode that was able to sustain the lithiation induced stress without undergoing pulverization. In addition, the electrode with such morphology provided better electrolyte accessibility and simultaneously ensured shorter Li^+ diffusion lengths.

To evaluate the practical behaviour of the electrode, the electrochemical characteristics of a full cell consisting of Ge anode and lithium cobalt oxide cathode was studied. At a current density of 1 mA/cm² the areal capacity at the end of 180 cycles was 0.68 mAh/cm² at CE of 99.6%.

Transmission electron microscopy (TEM) and selected area electron diffraction were used to study the electrode morphology before and after cycling and the phase transformation. The results indicated that the electrode stability resulted from the ability of the individual grains to keep the electrical contacts between them, even at big changes in the volume due to the lithiation.

Macroporous (MP) Ge@TiO_2 composite, consisting of nanoscale Ge network skeleton wrapped with TiO_2 particles was prepared by dealloying of $\text{Ge}_{4.5}\text{Ti}_{0.5}\text{Al}_{95}$ alloy via its immersion in 0.01 mol/L NaOH solutions at 25 °C for 4 h [8]. During the selective dissolution of Al, Ge atoms were brought together and formed three dimensional (3D) network nanostructure with high porosity. Meanwhile Ti atoms were oxidized and further (by a spontaneous aggregation) formed TiO_2 particles layer that covered the porous Ge surface.

In order to study the lithium storage performances of the prepared Ge@TiO_2 material, CR2032 coin-type cells were fabricated where Ge@TiO_2 -based material served as the anode active substance. Anodes with pure Ge as active material were also prepared for comparison. The other materials included in the slurry used to prepare anodes, besides the active materials, were Super P, and sodium alginate. Cu foil was used as current collector. The counter electrode was a lithium foil, and the separator – a microporous membrane. The electrolyte was 1 mol/L LiPF_6 dissolved in the mixture of EMC, DMC and EC (1:1:1 – a volume ratio) with an addition of 3 v.% vinylene carbonate (VC) that acts as film forming additive.

Studies on the cycling performances and CEs of Ge@TiO_2 anode and pure Ge anode were carried out at current density of 400 mA/g. The Ge@TiO_2 electrode provided a reversible capacity of 963 mAh/g after 100 cycles while the capacity of pure Ge was 418 mAh/g, thus suggesting the more stable lithium storage performances of the Ge@TiO_2 material.

The cycling performances of MP Ge@TiO_2 and pure Ge anodes at current density of 3200 mA/g were also studied. Ge@TiO_2 maintained reversible capacity of

716.7 mAh/g after 300 cycles, while the capacity of pure Ge electrode at the 300th cycle was 126.4 mAh/g. TEM images showed that the structure of pure Ge underwent serious fracture and collapse after cycling while the Ge/TiO₂ material preserved its original porous network architecture.

The rate performances of MP Ge@TiO₂ and pure Ge electrodes were studied, as well. The Ge@TiO₂ electrode exhibited specific discharge capacities of 1182.2, 1040.4, 955.3, 820.0, and 774.8 mAh/g at the current densities of 160, 400, 800, 1600 and 3200 mA/g, correspondingly. The pure Ge showed lower capacity at all current densities and a discharge capacity of only 134.6 mAh/g at 3200 mA/g. When the current density was back to 160 mA/g (after it was 3200 mA/g) the specific capacity for Ge@TiO₂ returned to 1036.5 mAh/g indicating very good rate performance.

The excellent characteristics of the prepared material were explained by its structure. The 3D macroporous network with its channels accelerates the movement of electrons and ions during lithiation/delithiation process. The robust TiO₂ layer ensures mechanical strength and prevents the direct contact between Ge and electrolytes, thus hindering the continuous increase of SEI which causes the capacity decrease.

2.2 Germanium oxide based nanomaterials

Due to its high theoretical capacity of 2152 mAh/g, in the case that it reversibly stores 8.4 Li⁺, GeO₂ is considered as an encouraging anode material for LIBs [9]. In addition, GeO₂ is cheaper than pure Ge. However, its fast implementation in LIBs is hindered by the GeO₂ poor electrical conductivity and the very big volume changes during the charge/discharge process, resulting in the degradation (pulverization) of the electrode material, unstable SEI and as a result poor performance. In an attempt to obtain novel GeO₂-based anode materials with enhanced performance, preparation of porous GeO₂ nanoparticles through thermal decomposition of (Hbipy)₂[Ge(C₂O₄)₃]·2H₂O in air atmosphere has been proposed [9]. The idea was to use the ability of porous structures to relax the mechanical strain resulting from the volume expansion during cyclic process, as well as their large surface area facilitating electrode-electrolyte interface, and thin walls ensuring fast diffusion of Li⁺.

The prepared porous GeO₂ nanoparticles possessed an average size of 200 nm, pores of 4 nm, BET surface area of 74.0 m²/g and total pore volume of 0.208 cm³/g.

When used as LIB's anode the materials exhibited a discharge capacity of 2578.8 mAh/g at current density of 100 mA/g. Even at current density of 2 A/g, the reversible specific capacity was 184.2 mAh/g. After the high-rate measurements, the specific reversible capacity was 727 mAh/g when the current density was set back to 100 mA/g. This finding points at good electrochemical reversibility and structure stability.

A comparison of commercial GeO₂ and the synthesized porous GeO₂ nanoparticles pointed at the superiority of the latter. After 100 cycles at 100 mA/g, the porous GeO₂ possessed a reversible capacity of 581.9

mAh/g for Li⁺ storage, while that of the commercial GeO₂ was 256.5 mAh/g. The good performance of the prepared material is assigned to the synergism of nanoscale, porous structure and low crystalline structures formed during the synthesis.

One-pot environmentally friendly synthesis of amorphous Ge oxide-carbon (GeO_x-C) hollow composite has been proposed by using citric acid (CA) as reductant of the germanium ions obtained by dissolving GeO₂ in NH₄OH [10]. The amount of the added reductant influenced the thickness of the resulting hollow structure, but the hollows' size of the GeO_x materials was not changed. Under the optimum ratio of CA to GeO₂ 13-16 nm shells were formed and this material showed the best electrochemical performance.

The LiB anode prepared using this material exhibited a capacity of 930 mAh/g after 100 cycles at rate of 0.3C, while the CE was 99.9%.

The cycling stability of the GeO_x-C hollow composite was studied by gradually applying C-rate from 0.1C to 10C. At that, the specific capacity of the sample slowly decreased from 956 to 612 mAh/g. Nevertheless, when 0.5 C was applied after 10C, the reversible capacity come back to 935 mAh/g showing a very good performance. The repetitive fast cycles charge/discharge' carried out at rate of 2C showed that after 400 cycles the reversible capacity was 757 mAh/g, (approximately 90% retention compared to the second cycle) pointing at good cycling stability.

It has been found that during the lithiation/delithiation process the thickness of the GeO_x-C hollow composite electrode changed by approximately 12%, while the thickness of an electrode prepared from commercial GeO₂ changed by up to 150%. The HRTEM analysis of the GeO_x-C hollow composite showed well preserved hollow structure and uniform distribution of Ge and O atoms even after 400 cycles.

The enhanced electrochemical performance of the GeO_x-C hollow composite was assigned to the synergistic effect of the hollow structure with optimized thickness of the shells, amorphous nature, and the presence of conductive carbon. The composite shell layers supplied a surface for formation of stable SEI layer by avoiding the direct contact between the electrolyte and the anode. Availability of an internal void space ensured free expansion of the anode material without increasing the volume of the entire electrode. All these features allowed for an effective accommodation of volume change and facilitated transport of electrons during charge/discharge process.

2.3 Germanium alloys-based nanomaterials

Germanium alloying represents one of the ways for mitigating/avoiding the structural pulverization and loss of electrical conduction paths between the active materials and current collector in LIBs' anodes. In line with these efforts free standing non-carbon electrodes were prepared by mixing Ge and Cu nanowires [11]. The electrodes were tested as anodes for LIBs. Half-cells (of CR2032 type) were prepared using as working electrode

the produced free standing NW fabric, Li metal foil was the counter electrode. The electrolyte was 1 M LiPF₆ in 3:7 (v/v) fluoroethylene carbonate/dimethyl carbonate (FEC/DMC) and it was loaded on a microporous PE separator. The material prepared under optimum conditions exhibited initial charge and discharge capacities of 1348 mAh/g and 1107 mAh/g corresponding to the CE of 82.1%. Its capacity retention was 80.3% after 50 cycles.

High-resolution SEM and TEM images of the electrodes before and after 100 cycles showed that before cycling Ge nanowires waved with each other into the fabric structure. The X-ray spectroscopy (EDS) of the contact point revealed that the atomic ratio of Cu to Ge was 3:2, which proved the formation of copper germanide. After cycling, the nanowire composites were coated by a uniform SEI layer.

The free standing NW fabric electrodes possess the following advantages for application in LIBs: (i) The elaborated electrode structure needs neither a metal foil current collector nor polymer binders in the production process. As a result, the whole electrode is considerably lighter than conventional electrodes made by slurry coating on metal foils; (ii) The existence of the raw material in the form of wires supplies many intersections between NWs (like 3D interconnectivity) leading to an accelerated electron transport; (iii) The space between the NWs can alleviate the volume changes during alloying and dealloying process and improve the electrolyte penetration leading to easier Li⁺ diffusion in the electrode.

The Cu content and the annealing temperature were found as the two main factors determining the electrochemical performance of the free standing NW anode electrodes.

Use of core-shell array nanostructures as LIBs' anodes is able to significantly improve the electrochemical performance, especially the high-rate capability. Cobalt-germanium core-shell nanowire array anode (Co-Ge CNA) was synthesized by template-free approach applying direct deposition of a Ge layer on the surface of the preliminary synthesized Co NW arrays [12]. RF-sputtering method was used.

To study the performance of the produced material as anode for LIBs, 2025 coin-type half cells were assembled with a metallic lithium foil as the counter electrode, 1M solution of LiPF₆ in EC / DMC (1:1 by volume) as electrolyte and polypropylene micro-porous film as a separator.

At a current density of 320 mA/g the initial discharge and charge capacities of Co-Ge CNA were 1994.8 and 1441.4 mAh/g correspondingly, resulting in an initial Coulombic efficiency (ICE) of 72.3%. The irreversible capacity loss in the first cycle is assigned to the SEI formation. In the further cycles the Co-Ge CNA anode exhibited practically constant capacity and it was 1535 mAh/g after 100 cycles.

The rate performance of Co-Ge CNA electrodes was studied under different current rates in the range of 0.2C – 5C. The discharge capacities of 1493, 1482, 1467, 1357 and 1239 mAh/g were recorded at 0.2, 0.5, 1, 2 and 5C (= 8000 mA/g), correspondingly. However, when

again a current of 0.2C was applied, the Co-Ge CNA electrodes showed a capacity of ~1446 mAh/g and a stable cycling performance. The good rate performance is assigned to the core-shell array nanostructures that are able to provide vigorous mechanical support, fast electron transport, and improved contact to the current collector.

2.4 Nanocomposites of germanium and carbon-based materials

Composites consisting of Ge NPs and carbon-based materials continue to be considered among the most promising materials for preparation of LIBs' anodes, since carbon coating on Ge particles acts as a buffer layer effectively limiting volume expansion and aggregation of Ge NPs. In comparison with amorphous carbon coating, the ordered mesoporous carbon (OMC) in addition to providing large surface area, uniform pore size and good conductivity, can be used as a matrix that contains electroactive material, exercising a confining effect and maintaining the integral structure. Combining Ge nanoparticles with the advantages of ordered mesoporous structure is considered as a plausible strategy for the synthesis of high-capacity, long-cycle life electrode materials.

A composite consisting of Ge NPs embedded in spherical ordered mesoporous carbon (S-OMC/Ge) was prepared by impregnating the ammonium salt of Ge in the pores of OMC, followed by high temperature pyrolysis and H₂ reduction [13].

The electrochemical performance of the synthesized composite as an active anode material was tested by preparing CR 2032 coin cells. The anode contained the active material, acetylene black, and binder polyvinylidene fluoride (PVDF) at a mass ratio of 75:15:10, the current collector was Cu foil. A lithium plate was the counter electrode, and the electrolyte was 1.0M LiPF₆ in EC – DEC at ratio 1:1 vol.%.

The cycling behaviour of S-OMC/Ge based electrodes as well as of electrodes based on pure spherical OMC (S-OMC) and pure Ge materials were studied in 160 cycles at the current density of 100 mA/g. The capacity of S-OMC sample was 643 mAh/g after 160 cycles. The capacity of Ge electrode was 173 mAh/g after 3 cycles, showing a rather poor cycling performance. The composite S-OMC/Ge sample exhibited a stable circulation in the 160 cycles, with capacity of 996 mAh/g.

The rate performance of the S-OMC/Ge electrode was evaluated by applying different current densities. The measured reversible discharge capacities were 1025, 934, 807 and 681 mAh/g at applied current densities of 100, 200, 500 and 1000 mA/g, correspondingly. When the applied current density was returned to 100 mA/g, the reversible capacity was stabilized at 890 mAh/g after 60 cycles. The reversible capacities measured under the same conditions for S-OMC and pure Ge samples were much worse. The cycle stability of S-OMC/Ge electrode was studied also at high current density of 1 A/g. The

electrode maintained a reversible capacity of 530 mAh/g after 200 cycles and the CE was stable, at 99.2%.

The proposed explanation of the high capacity of S-OMC/Ge composite was by the complete structure formed by Ge particles (that possess a high theoretical capacity) even distribution in the mesoporous carbon.

It was found that the content of Ge had an effect on the performance of S-OMC/Ge composites. The low Ge content was not enough to ensure the impact of the Ge high theoretical capacity, while use excessive Ge lead to Ge agglomeration and blocking of the mesoporous carbon pores, which affected the overall performance of S-OMC/Ge composite.

The good performance of the prepared composite is assigned to the synergistic effect between the support of spherical OMC and the high capacity provided by dispersed Ge particles. The spherical ordered mesoporous carbon supplies channels able to alleviate the volume changes during the lithiation / delithiation cycling and ensures high electrical conductivity.

Decreasing the aggregation of Ge NPs occurring during electrodes' cycling represents another direction for improving the properties of Ge NPs based anodes for LIBs. NPs' anchoring on conductive substrates, such as graphene (Gr), CNTs, and RGO or NPs encapsulation in hollow carbon active material is accepted as the problem's solution. These carbon materials prevent large volumetric expansion thus ensuring long-term stability and high electrical conductivity resulting in high power of the batteries.

The reactive sites of nitrogen doped single walled carbon nanohorns (N-SWCNHs) were utilized by favourably growing of germanium nanocrystals (Ge NCs) onto their conical tips by applying oleylamine as a reducing agent [14]. The prepared Ge@N-SWCNHs composite was studied as an active anode material for LIBs. For this purpose CR2032 coin cells were elaborated with Li chips as reference and counter electrode, the separator was dried glass fibers membrane and the working electrode was Ge@N-SWCNHs composite, casted on a copper foil. The slurry casted on the foil consisted of 70 wt.% Ge@N-SWCNHs composite (containing 70 wt.% Ge), 20% Super-P carbon and 10% PVDF in N-methyl-2-pyrrolidone (NMP). The electrolyte was 1 M LiPF₆ dissolved in 1:1 mixture of EC and DMC with 5 v.% of VC as an additive.

The capacity of Ge@N-SWCNHs composite based electrode after 5 cycles stabilized at 1435 mAh/g while for an electrode based on Ge NCs as an active material the capacity was 1046 mAh/g. The higher capacities obtained for Ge@N-SWCNHs composites were assigned to the lower activation energies permitting entire utilization of active material. The capacity retention of electrodes based on Ge NCs and Ge@NSWCNHs composites was tested for over 100 cycles. Pristine Ge NCs and Ge@N-SWCNHs composites showed stable discharge capacities of 811 and 1285 mAh/g after 100 cycles, correspondingly. The main part of the delithiation capacity in Ge@N-SWCNHs composite was lost during the initial 10 cycles (6%) while the loss was 2.5% for the remaining 90 cycles. The CE of Ge@N-

SWCNHs composite after 20th cycle was higher than 95%, and for the 80th cycle it was practically 100%.

The rate behaviour of Ge@SWCNHs composite was studied at various charge / discharge rates and compared with the behaviour of Ge NCs and of pristine NSWCNHs under the same conditions. At rates of 0.1C, 0.4C, 0.8C, 1C, 2C and 5C the capacity of Ge@N-SWCNHs composite based electrodes was 1420, 1193, 935, 866, 611, 366 mAh/g, correspondingly. The capacity of Ge NCs based electrodes was 908, 762, 599, 462, and 271 mAh/g at 0.1C, 0.4C, 1C, 2C and 5C correspondingly, while the capacity of pristine NSWCNHs was 48, 36, 26, 15 and 9 mAh/g at 0.2C, 0.4C, 0.6C, 0.8C and 1C respectively. When after applying the highest discharge rate, it was returned to 0.1C, the capacity of Ge NCs based electrode was 850 mAh/g, while the Ge@SWCNHs based electrode recovered its original capacity of 1413 mAh/g.

The high storage capacities and the excellent rate behaviour of Ge@N-SWCNHs were assigned to the very good contact between Ge NCs and N-SWCNHs leading to high utilization of the active material. The preferential growth of Ge NCs on the tips of N-SWCNHs averts the NCs aggregation after many charge/discharge cycles.

Production of N-SWCNHs is relatively cheap and scalable and this makes the synthesized composite a promising candidate for LIBs anodes.

A layered germanium phosphide (GeP₃) – carbon black nanocomposite was prepared by high-power ball-milling technique [15]. The nanocomposite was tested as active material for LIBs anode. A button-type electrochemical half cell was assembled where Li metal was applied as the counter and reference electrodes, the separator was Celgard 2400 membrane, and electrolyte was 1 M LiPF₆ dissolved in EC – DEC (1:1 by volume), containing 5% fluorethylene. The electrode exhibited a capacity of 1450 mAh/g after 30 cycles at rate of 100 mA/g. At high current (1900 mA/g) the capacity was 860 mAh/g. The CE was in the range 87 – 93% after 100 cycles. The observed good electrochemical and cycling performances were assigned to the presence of very small GeP₃ nanocrystallites (3–5 nm) in the amorphous C matrix and to the created short Li⁺ ion diffusion paths.

Recently Ge coating for a 3D porous carbon on the surface of Ni foam has been prepared by ionic liquid electrodeposition followed by annealing [16]. Thus a 3DVoid/Ge@C composite has been produced. The material has been tested as a LIB anode. At current densities of 0.1, 0.2, 0.5, 1, and 2 A/g, the electrode has shown a reversible specific capacity of 1592.9, 1054.9, 921.3, 771.4, and 471.2 mAh/g, correspondingly. The good performance of the prepared material has been ascribed to (a) the elasticity of the carbon sheet that facilitates the contact with Ge nanoparticles and protects pathways for the Li-ions transport and (b) the created 3D micro-nano void structure that decreases the damage from large volume changes during the intercalation and deintercalation process of Li⁺ ions.

Three-dimensional nitrogen-doped graphene foam (NGF) has been prepared that contained interconnected pores and encapsulated Ge quantum dots. The obtained material was covered with polydimethylsiloxane to

produce yolk-shell nanoarchitecture [17]. The material performance was tested by preparing two-electrode CR2025-type coin cells. The separator was porous polypropylene film, lithium foil was used as the counter electrode and 1M solution of LiPF_6 in the mixture EC – DMC – DEC (at volumetric ratio of 1:1:1) was used as an electrolyte. Thus prepared nanocomposite (Ge-QD@NG/NGF/PDMS) showed a reversible capacity of 1220 mAh/g at current of 1600 mA/g, preserved for 1000 cycles. The material exhibited high rate capability of more than 800 mAh/g at current of 64 A/g and 200 cycles. The averaged coulombic efficiency was 99.7% for the studied 1000 cycles. The excellent behavior of the prepared nanocomposite is assigned to the creation of internal void space that ensured better relieving the volume expansion during lithiation. In addition, the N-doped graphene outer shell decreased significantly the exfoliation, pulverisation and aggregation of Ge. The elaborated material is suitable for preparing flexible electrodes.

In an attempt to overcome the negative effect of volume changes during the charging/discharging and the aggregation of Ge particles, a core-shell structured germanium@carbon (Ge@C) NPs were homogeneously anchored on the RGO nanosheets to obtain Ge@C/RGO hybrid [18]. Initially Ge NPs were prepared by a mechanochemical reaction between GeO_2 and Mg powders. Further, Ge NPs were coated with polydopamine films, thus core-shell structured germanium@polydopamine (Ge@PDA) composite was prepared. The next step was the Ge@PDA anchoring on the graphite oxide (GO) making use of the dopamine strong adhesion, followed by calcination to form the Ge@C/RGO hybrids.

The electrochemical behavior of the prepared composite was studied using CR2025 coin-type cells in which working electrode consisted of active material (namely Ge@C/RGO, as well as Ge@C – for comparison), Super P, and lithium polyacrylate at weight ratio of 8:1:1, mixed with deionized water to form homogeneous slurry. Further, Cu foil, serving as a current collector, was coated with the slurry, cast in disks and dried. Li metal was used for counter and reference electrodes, and glass fiber for separator. The electrolyte was 1 M LiPF_6 dissolved in EC – DMC (1:1 by volume) with and addition of 5 wt.% fluoride ethylene carbonate (FEC).

Initially charge and discharge specific capacities were 1692.3 and 1258.5 mAh/g at C/10 (the current density of 1C rate was 1600 mA/g), corresponding to an ICE of 74.4%. This low ICE was assigned to decomposition of electrolyte and SEI formation. The initial discharge and charge capacity of the Ge@C, under the same conditions, were 1495.3 and 1252.1 mAh/g, correspondingly. The higher ICE of the Ge@C compared to the Ge@C/RGO was explained by the higher specific surface area of the latter leading to more surface side reactions and thicker SEI layers. After the second cycle, the CE of Ge@C/RGO electrode reached over 98% and kept at that value for up to 600 cycles.

The reversible capacity of Ge@C/RGO electrode after 600 cycles at discharge rate of 2C was 1074.4

mAh/g, which is 96.5% of the capacity at the 2nd cycle at 2C. For comparison, the reversible capacity of the Ge@C electrode after 600 cycles at 2C was 362.6 mAh/g indicating that only amorphous carbon layers cannot ensure stable long-term cycling performance.

Results from SEM and TEM analyses showed that after 600 discharging / charging cycles the Ge@C electrode suffers from significant pulverization and most of the active materials have lost contact with the current collector. Under the same conditions the Ge@C/RGO based electrode kept its surface morphology and structural stability. This is assigned to the high elasticity of RGO which was able to buffer the stress generated during the lithiation / delithiation of Ge.

The rate capability of Ge@C/RGO and Ge@C electrodes was studied at different current densities. At the rates of 5C, 10C, 15C, and 20C the Ge@C/RGO electrode exhibited reversible capacities of 1319.0, 1104.1, 879.4, and 711.6 mAh/g respectively. Under the same current densities, the Ge@C electrode reversible capacities were 988.9, 511.0, 293.1 and 204.3 mAh/g, respectively. When the rate was decreased to 0.2C the both electrodes recovered high capacity. After 200 cycles of lithiation/delithiation, no significant drop of capacity was observed at rates from 1C to 10C. The specific capacity of Ge@C/RGO electrode after 200 cycles decreased to 436 mAh/g at rate of 20C. However, this is still higher than the theoretical capacity of graphite anode (372 mAh/g).

The excellent rate performance of the Ge@C/RGO electrode is assigned to the double carbon matrix composed of amorphous carbon and RGO nanosheets. The carbon layers ensure conductive pathways for diffusion of electrons and Li^+ . The homogeneous and continuous carbon layers in the core-shell structured Ge@C composite alleviate the large volume changes of Ge during lithiation / delithiation and improve the conductivity of Ge electrode. The uniform anchoring of the core-shell structured Ge@C particles onto the surface of RGO decreases the agglomeration of Ge@C composites and betters the active materials' utilization. The highly flexible RGO nanosheets decrease the stress resulting from the multiple volume changes and enhance the structural stability of electrode during cycling. In addition, Gr nanosheets and carbon shells create a hybrid conductive matrix, which improves the electronic conductivity and minimizes the volume change of Ge.

Similarly, a double-layered protective structure was synthesized in which the hollow cubic Ge@C hybrids were evenly dispersed on RGO sheets, thus forming Ge@C-RGO composite [19]. To prepare the composite Ge-bearing precursor ($\text{NH}_4\text{H}_3\text{Ge}_2\text{O}_6$) was dopamine-coated and further subjected to carbothermal reduction processes to obtain a Ge@C composite where the carbon is N-doped. Further, the cubic Ge@C was dispersed on the RGO. The RGO along with the carbon layer formed a double carbon layer structure protecting Ge particles.

The electrochemical properties of the as-prepared material were studied using CR2032 coin-type cells. The Ge@C-RGO composite was applied as an active material. It was mixed with conductive carbon black and the binder (PVDF) at a mass ratio of 80:10:10, and

dissolved in NMP to prepare a suspension, cast on a Cu foil (current collector). Thus prepared system was used as an anode, Li metal was the counter electrode and the electrolyte was 1.0M LiPF₆ in EC – DEC (1:1 by volume) and 5 wt.% FEC. For comparative purposes, cells using Ge@C or Ge as active anode material were also prepared and studied.

It was found that the discharge capacities of Ge@C-RGO, Ge@C and Ge electrodes at 100 mA/g for 200 cycles were 1183, 567 and 202 mAh/g, correspondingly. The reversible capacity of Ge@C-RGO based electrode at current of 1 A/g for 200 cycles was 710 mAh/g, and the CE reached 99.30%.

The rate capability was studied at specific currents of 100, 200, 500 and 1000 mA/g. The capacities delivered by Ge@C-RGO were 999, 796, 718, and 664 mAh/g correspondingly, while the Ge@C electrode exhibited capacities of 589, 540, 461 and 418 mAh/g under the same conditions. When the specific current returned back to 100 mA/g, the capacities were 991 and 576 mAh/g for Ge@C-RGO and Ge@C respectively, indicating good reversibility of the both electrodes. At the same time, the pure Ge electrode showed a continuous decline in capacity at each current rate, indicating its poor electrochemical stability.

The outstanding electrochemical performance of the Ge@C-RGO based electrode is assigned to the formation of a double-carbon layer protective structure in which the hollow cubic Ge@C hybrids are evenly dispersed on the graphene sheets. The connected carbon shells, as a support structure, keep the shape of the material, alleviating the changes during the cycling, and the Ge@C core-shell structure ensures space for the volume expansion of Ge particles. RGO as a supporting substrate ensures good dispersion and fixation of Ge@C hybrids and with its large-area and high-flexibility buffers the stress caused by volume changes during charging / discharging. The N-doped carbon shell and the graphene network speed-up the transport of Li⁺. The dispersed small Ge nanoparticles shorten the Li⁺ transport path. The both effects contribute to the improved overall conductivity of Ge@C-RGO electrode.

Chen and coauthors reported in situ synthesis of Ge/RGO composites using GeO₂, as Ge source and NaBH₄ as reductant. The process was assisted by a cationic polymer – poly(diallyldimethylammonium chloride [20]. In this synthesis GeO₃²⁻ anions were adsorbed on cationic polymer-modified graphene oxide sheets by means of an electrostatic interaction. Further, in-situ reduction was carried out leading to the formation of ultrafine Ge nanoparticles (ca. 5 nm) on RGO sheets thus creating uniform sandwich-like structure.

The prepared composite was studied as an active material for LIB, using two-electrode CR2032-type coin cells. Besides the prepared composite, the working electrodes contained conductive agent (acetylene black) and binder carboxymethyl cellulose sodium at weight ratio of 8:1:1. The mixture was dispersed in deionized water and thus formed homogeneous slurry was uniformly coated onto pure Cu foil (serving as current collector), dried and cut into disks used as the working electrodes. Lithium foil was applied as both reference

and counter electrodes. The electrolyte was 1.0M LiPF₆ dissolved in EC – DMC (1:1 by volume) containing 5 wt. % FEC. A full Li-ion cell was also prepared with a cathode, based on commercial LiFePO₄. The LiFePO₄ electrode was made by mixing 80 wt % of LiFePO₄, 10 wt% of acetylene black and 10 wt % of PVDF in NMP. Further, the slurry was spread on an Al foil and dried. Before fabricating the full cell, the Ge/RGO anode was pre-lithiated by placing it in direct contact with a lithium foil in the presence of the cell electrolyte.

It was found that the amount of used RGO influences the electrochemical behavior of the Ge/RGO composite. For the composite with the optimal RGO content the initial charge and discharge specific capacities were 2100 and 1184 mAh/g respectively, resulting in an ICE of 56.4%. The relatively low ICE was assigned to the formation of SEI films. The CE increased to ca. 95.0% at the 3rd cycle, and after 5th cycle became above 99.0% and remained at that value after the 100 cycles at current density of 0.2 A/g.

After 100 cycles the Ge/RGO-based electrode exhibited discharge capacity of approximately 960 mAh/g at 0.2 A/g, while the specific capacity of the prepared for comparative purposes pristine Ge-based electrode was 503 mAh/g after 100 cycles. The improved specific capacity of Ge/RGO-based electrode was explained with the high electrical conductivity and large specific surface area of the RGO matrix.

The rate performance was studied at different current densities. The specific capacities of Ge/RGO based electrode at 0.1, 0.2, 0.4, 0.8, 1, 2 and 5 A/g were 1290, 1194, 1112, 1036, 985, 877 and 631 mAh/g, correspondingly, while (for comparison) the specific capacity of pure Ge was 141 mAh/g at 5 A/g. When the current density of Ge/RGO based electrode was returned back to 0.2 A/g, the reversible capacity recovered to 1177 mAh/g.

The long-term cycling behavior of the Ge/RGO based electrode with the optimal RGO content was assessed at a current density of 1 A/g. The initial discharge capacity was 940 mAh/g, and it was 705 mAh/g after 350 cycles. Even at a high discharge rate of 5 A/g the reversible capacity of the Ge/RGO based electrode was 480 mAh/g after 250 cycles.

Furthermore, the coin-type full cell with the Ge/RGO composite as anode and commercial LiFePO₄ as cathode (at 85 mA/g) delivered an initial charge capacity of 149 mAh/g and discharge capacity of 131 mAh/g, which corresponds to the ICE of 87.9%.

The full cell still possessed a good cycling stability with a specific capacity of 120 mAh/g after 100 cycles at 0.5C. The Ge/RGO//LiFePO₄ full cell showed reversible capacities of 156, 152, 134, 115, 95, 62, 41 and 16 mAh/g at 0.1C, 0.2C, 0.5C, 1C, 2C, 5C, 10C and 15C, correspondingly. When, after the high current discharge, the rate was returned back to 0.2C, the capacity measured was 151 mAh/g. These findings point at the applicability of the Ge/RGO composite as anode in commercial LIBs.

The outstanding electrochemical performance of Ge/RGO composite is assigned to the elaborated nanostructure and to the resulting synergistic effect

between Ge NPs and RGO sheets. The two-dimensional structure and large surface area of the RGO facilitates the uniform dispersion of Ge NPs in RGO matrix, prevents their agglomeration and ensures more active sites for lithium storage. The Ge/RGO composite supplies enough void space to buffer the volume change of Ge and maintain high structural stability during cycling. RGO (when in optimal concentrations) with its high electrical conductivity promotes the electron transport. Its large area ensures better contact with the electrolyte and shortens the transport distance of Li^+ ions thus contributing to the superior rate capability.

Very recently germanene-reduced graphene oxide GeCH_3/RGO nanocomposites have been synthesized and studied as anode materials for LIBs by using home-made 2032 cells [21]. The counter electrode was lithium metal, the separator – Celgard 3500 membrane and the electrolyte – 1 M LiPF_6 dissolved in an EC – DEC – DMC mixture (at 1: 1: 1 in volume) with 2% FEC. The results revealed that the reversible capacity of the material prepared with 30 wt% RGO content (the optimum composition) used as anode was 1195 mAh/g after 5 cycles, and even after 100 cycles it was 1058 mAh/g showing a stable work. The CE was 98%. Even after 500 cycles, the capacities of the material with optimal composition were 439 and 288 mAh/g at current densities of 0.5 A/g and 1 A/g correspondingly, and the respective CE were 98.58% and 99.31%.

Only several months ago a material based on mixed Ge oxide and RGO has been presented [22]. The $\text{CuGeO}_3/\text{RGO}$ nanocomposite makes use of high capacity possessed by CuGeO_3 and stable framework created by the RGO. Thus prepared composite was tested as anode active material for LIBs electrodes. The electrode was made of 80 wt% $\text{CuGeO}_3/\text{RGO}$, 10 wt% conductive acetylene black and 10 wt% binder (PVDF). CR2032-type coin half cells were prepared. The counter electrode was metallic Li and the electrolyte consisted of LiPF_6 dissolved in EC – DEC (at ratio 1:1) with addition of 5 vol% of FEC. It has been found that composite $\text{CuGeO}_3/\text{RGO}$ containing 30 wt% GO exhibits very good electrochemical performance. It possessed a reversible capacity of 909 mAh/g and high CE of 91.49% at the current density of 100 mA/g after 200 cycles. The specific capacities of the prepared composite were 709.4 mAh/g, 609.7 mAh/g and 523.4 mAh/g when it was cycled successively at 200 mA/g, 500 mA/g and 1000 mA/g. At restoration of the current density to 100 mA/g, the capacity recovered to 747.6 mAh/g. The good electrochemical characteristics of the $\text{CuGeO}_3/\text{RGO}$ composite were assigned to the combined effect of the crystalline CuGeO_3 nanorods and RGO sheets framework. The CuGeO_3 nanorods ensure direct transport tunnels for lithium ions, while the RGO sheets supply a stable conductive network having large specific surface area for even dispersion of the CuGeO_3 . In addition, the RGO skeleton restricts the excess volume expansion of CuGeO_3 , thus preventing the pulverization of the electrode during the lithiation/delithiation process.

A brief summary of the studies carried out in the recent 3–4 years on Ge-based nanomaterials preparation

and testing as anode materials for LIBs is presented in Table 1.

Table 1. Brief summary of the recent 3-4 years studies on Ge-based nanomaterials for LIBs anodes.

Material	Capacity, mAh/g	Current density, mA/g	Charge-discharge cycles demonstrated	Ref.
Ge NWs	884	320	50	5
Ge/3DOM-Ni	610	320	100	6
Porous Ge	649 (1300)	8000 (1000)	1800 (340)	7
Ge@TiO ₂ composite	963 (717)	400 (3200)	100 (300)	8
GeO ₂ NPs	582	100	100	9
GeO _x -C composite	930 (757)	630 (4200)	100 (400)	10
Ge NW/ Cu NW composite	889	1300	50	11
Co-Ge core-shell NW array	1535 (1239)	320 (8000)	100 (45)	12
S-OMC/ Ge	996 (530)	100 (1000)	160 (200)	13
Ge@N-SWCNHs composite	1285 (866)	160 (1600)	100	14
GeP ₃ -C black composite	860 (1450)	1900 (100)	100 (30)	15
3DVoid/Ge@C	990 (1300)	100 (100)	100 (10)	16
Ge-QD@ NG/NGF/PDMS	1220 (800)	1600 (64000)	1000 (200)	17
Ge@C/ RGO hybrid	1074.4	3200	600	18
Ge@C-RGO hybrid	1183 (710)	100 (1000)	200 (200)	19
Ge/RGO composite	960 (705 and 631)	200 (1000 and 5000)	100 (350)	20
GeCH ₃ / RGO composite	1058 (439)	200 (500)	100 (500)	21
CuGeO ₃ /RGO composite	909 (523)	100 (1000)	200 (40)	22

3 Conclusions and outlook

As a conclusion it can be said that Ge NPs, Ge nanoalloys and Ge-based nanocomposites have been and are being widely studied for their ability to serve as advanced anodes in LIBs. These materials allow overcoming the problems related to volume expansion / contraction during the lithiation / delithiation reaction, while ensuring high reversible capacity and high rate under the applied test conditions.

However, studies on the cycling performance of the electrodes, based on the developed materials, seldom reach the cycles of the commercially used batteries. Further investigations in this direction are needed, with higher number of charge / discharge cycles.

Most of the cells assembled with the developed anodes resemble primary cells, the studies using as counter-electrode materials applied in real LIBs are very scarce. Studies of whole cells where the developed

materials are working with cathodes based on commercially used materials are highly needed.

Efforts must be continued to find the conditions for convenient production of large quantities of nanomaterials for the preparation and testing of larger batteries, rather than individual electrochemical cells.

Finally, we can say that Ga-based nanomaterials are promising active matter for advanced anodes for LIBs but still much work is required for their implementation in the commercial batteries.

In addition, since the sodium ions cannot intercalate into graphite in a reversible manner, the Ge-based nanomaterials deserve more attention as eventual anodes for sodium-ion battery.

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