

Final report

**Nano-scaled structures for electrochemical
energy storage in autonomous
microsystems**

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1. Project overview

The emergence of micro- or nano-electromechanical systems (MEMS/NEMS) has led to the development of a variety of autonomous microdevices, such as biomedical sensors, wireless sensors and actuators. To enable an on-board power delivery in these microelectronic devices, miniaturized energy-storage systems are highly demanded as they are able to facilitate the integration process. However, the realization of such energy storage units is fundamentally limited by the development of batteries or supercapacitors on the nanometer scale, where a different design is required to the bulk counterparts. In addition, the working mechanisms and especially degradation phenomena are also different and call for a revision of the underlying concepts and the selection of specific materials. Specifically, the development of an optimized nano-structured electrochemical energy-storage system requires fundamental knowledge about the peculiar processes for ionic and electronic transport not only within the nanoparticles, but also through interfaces between them. This proposal addresses fundamental questions related to the transport behaviour and interactions in nano-scaled composite materials for energy storage in autonomous microsystems.

The project is composed of 4 work packages with contribution from all 5 institutes at the IFW Dresden.

Work Packages		Participating Institutes				
		IFF	IIN	IKM	IMW	ITF
WP1	Preparation of nanoparticles and nanostructures for electrodes		●	●		
WP2	Thin-layered electrode design		●	●		
WP3	Integration of components to energy-storage cells & determination of their performance		●	●		
WP4	In situ characterization, stability and transport properties of nanostructured materials	●	●	●	●	●

2. Achieved goals

The aim of this project is to develop new preparation methods for miniaturized energy-storage systems. This includes i) the synthesis of nano-structured composites and ii) their integration in a fully operational device. In order to reach optimum performance, it is necessary to analyse the resulting behaviour and to interpret it in terms of fundamental materials properties. This further understanding of materials interactions on the nano-scale will open new possibilities for autonomous microsystems with “on-board” energy supply and also improve nano-composite structures for bulk materials with better kinetics and higher capacities. The improvement of dedicated methods for the investigation of fundamental properties of functional materials on the nanometer scale will further strengthen the key competence of the IFW Dresden in this field.

The main achieved goals are summarized as follows:

- 1) Various nanostructures, such as nanotubes, porous nanoparticles, nanowires etc., are successfully prepared via sol-gel method, hydrothermal synthesis, and electrochemical deposition and so on.
- 2) Based on physical vapour deposition techniques (i.e. electron-beam evaporation, magnetron sputtering deposition), diverse thin films and their combinations are successfully deposited on different substrates.
- 3) Rolled-up nanotechnology is demonstrated to fabricate bulk strain-released microtubes with unique properties.
- 4) Employing these nanostructured materials as active materials for the electrodes, remarkable electrochemical performance have been achieved in battery cells, for instance, ultra-long cycle, high specific capacity and robust rate capability.
- 5) The underlying mechanisms for the degradation/improvement of battery performance have been identified via advanced techniques, e.g. EDX mapping, focused-ion beam (FIB) cutting, AES analysis.
- 6) In situ characterization of these nanostructured materials are performed.
- 7) The development of micro-scale energy storage devices are triggered for the application in autonomous microsystems.

3. Project methodologies, results and achievements

The purpose of this section is to summarize the developments that took place within the Pakt2011 project and put them in a larger scientific and technological context. We start with an overview of the preparation of nanostructured materials. Followed by the morphology and composition characterization, these nanostructured materials are fabricated in electrodes, which are then integrated with other active components for electrochemical measurements as battery cells or supercapacitors. Rolled-up nanotechnology, in many ways pioneered by IIN, IFW-Dresden, is proposed as the core strategy for the integration of micro-scale energy storage devices in this project. The resulted rolled-up nanomembrane electrodes will be described in details in the second subsection, and the electrochemical results will be analysed by a series of analytical techniques in collaboration with other institutes. With the attempt to gain a deep understanding of the underneath mechanisms for the degradation/improvement of battery performance, *in situ* characterizations are performed. The corresponding results are summarized in the third subsection.

3.1 Preparation of nanoparticles and nanostructures for electrodes

1) Hydrothermal synthesis for the MoS₂/PANI nanowires

As a typical layered transition-metal sulfide, MoS₂ has a structure analogous to that of graphite, in which S–Mo–S layers are held together by van der Waals forces. Such structure facilitates reversible Li⁺ intercalation/extraction, which enables MoS₂ to be a good electrode material for LIBs. Strongly dependent on their morphology and size, the reversible capacity of MoS₂ is obviously improved as nanoparticles or nanosheets are integrated on carbonaceous templates, suggesting the importance of hierarchical architectures. In this work, the hierarchical structure of polyaniline (PANI), in which MoS₂ nanosheets are evenly embedded in the PANI matrix, is developed for novel electrode materials with improved electrochemical performances. This novel structure is confirmed with SEM and TEM images, and the elements composition was characterized by XRD and IR measurements. The as-obtained MoS₂/PANI nanowires are significant for their hierarchical nanostructures integrated with 2D MoS₂ building blocks, in which MoS₂-PANI composition is well-defined by initial ratios of the precursors. These unique MoS₂/PANI nanowires exhibit greatly improved lithium storage properties owing to the hierarchical textures and the PANI-hybrid structures. MoS₂/PANI-II nanowires with the optimal composition (MoS₂ 66.7%: PANI 33.1%) display a high charge capacity of 1063.9 mAh/g at a current density of 100 mA/g, retaining 90.2% of the initial reversible capacity after 50 cycles. These results clearly demonstrate the advantage of the PANI-hybrid hierarchical structures, and further point out a new protocol for developing electrode-materials based on organic–

inorganic nanohybrids. [1]

3.2 Nanomembrane electrodes for electrochemical energy storage

Two-dimensional (2D) nanomembranes are of great interest for energy storage, in particular lithium-ion batteries, due to its shortened paths for fast lithium ion diffusion and large exposed surface offering more lithium-insertion channels. Their competitive lithium-storage features provide huge potentials to develop next-generation high-performance lithium-ion batteries. Therefore, various synthetic routes are highly desirable to fabricate 2D nanostructures for high performance LIBs. Moreover, nanomembrane-based thin film batteries dominate in micro-batteries, which make it even more important to investigate the nanomembrane electrodes, thus could be potentially applied in autonomous microsystems. Rolled-up nanotechnology is a method employing strain engineering to change thin film in-plane dimensions. Because of stresses generated during film deposition, the stress (strain) gradient through the film thickness causes bending of the film upon release from the substrate. The thin film rolls up into a tubular structure if the film length is longer than one circumference along the rolling direction. With a 3D configuration, these nanomembranes could reserve the advantages from thin films, but also present unique properties that are demonstrated to be helpful for the enhancement of battery performance.

1) Rolled-up composite microtubes for lithium storage

Hybrid multilayer Ge/Ti nanomembranes

Based on the rolled-up nanotechnology, composite “swiss roll” microtubes composed of multilayer germanium and titanium nanomembranes with superior reversible capacity are fabricated. Ge and Ti nanomembranes were deposited onto a silicon wafer via electron beam evaporation method and the tubular microstructures were fabricated via the release of the intrinsic strain accommodated in the nano-bilayer, which then results in a self-rolling delamination process. The whole process is highly efficient and also minimizes the whole system energy that leads to good volume tolerance during repeated charge/discharge cycles. These hybrid multilayer microtubes thus show a remarkably enhanced reversible capacity up to 1495 mAh/g with a high first-cycle Coulombic efficiency of 85%, and demonstrate an excellent capacity of ~930mAh/g after 100 cycles. The much improved capacity benefits from the unique structural features of the as-prepared hybrid multilayer Ge/Ti microtubes. The spatial confinement of the Ge microtubes by the surrounding Ti multilayers as a rigid frame/backbone stabilizes the electrode structure and limits the volume expansion upon lithium insertion/extraction, therefore preventing the pulverization of the active materials.

This work demonstrates that our bottom-up approach overcomes existing challenges and provides a new avenue for rational design of high-capacity hybrid nanomembranes to attain functionality currently unavailable in individual components for high performance energy storage devices.[2]

Naturally rolled C/Si/C trilayer nanotubes

Silicon has been extensively studied owing to its highest theoretical capacity (4200mAh g^{-1}), abundance in nature, low cost, and nontoxicity. However, Si-based anodes are notoriously plagued by poor capacity retention resulting from large volume changes during alloy/de-alloy processes (400%). The intrinsic strain generated during such expansion and contraction easily leads to electrode pulverization and capacity fading. Thus, it is a big challenge to achieve both excellent cyclability and enhanced capacity of Si-based anode materials. With the same method, a new type of tubular configuration was made from naturally rolled-up C/Si/C trilayer nanomembranes prepared via magnetron sputtering deposition. SEM images and Raman characterization prove the trilayered tube-wall configuration and element composition, respectively. Employing these nanomembranes as anode materials for lithium storage, a high capacity of $\sim 2000\text{mAh g}^{-1}$ can be retained at a current density of 50mA g^{-1} without discernible decay, and the capacity can keep $\sim 1000\text{mAh g}^{-1}$ even after 300 cycles at 500mA g^{-1} with almost 100 % capacity retention. The trilayer structure design provides a stable conductive network and prevents Si pulverization and aggregation during cycling, thus guaranteeing superior electrochemical performance. Moreover, the intrinsic strain accommodated in multi-layer nanomembranes is efficiently released by self-winding and thus offers a minimization of the system energy. Within this project, this work was performed in close cooperation with the scientists from IKM, IFW-Dresden. Particularly, Auger electron spectroscopy (AES) sputter depth profiling performed on the first delithiated C/Si/C microtubes revealed that the carbon coating in the C/Si/C microtubes does not break during the lithiation/delithiation. This further proves the robust structure stability and superiority for nanomembranes in lithium storage.[3]

Hierarchical $\text{SiO}_x/\text{SiO}_y$ bilayer nanomembranes

Except for the composite nanomembranes composed of different functional layers, a further develop on hierarchically designed $\text{SiO}_x/\text{SiO}_y$ bilayer nanomembranes are investigated as stable anodes for lithium ion batteries. In this work, a hierarchical electrode design with just one material SiO_x for distinct functionalities by controlling the oxygen content x in each layer. With a SEM image and a TEM image of the FIB-cut cross-section of a single rolled-up microtube, it clearly shows the interface between the silicon-rich and oxygen-rich layers. Energy-dispersive X-ray spectroscopy (EDX) was performed to map the element distributions in a single tube, the results clearly indicate a uniform distribution of both Si and O elements, which suggests that any strain generated by Si lithiation should be evenly distributed. An EDX line scan was also performed

on the cross section of a single tube by using Tecnai TEM, from which one can clearly identify the silicon-rich, oxygen-rich regions by following the Si and O signal variations as well as the O/Si intensity ratio along the line scan. The resulted SiO_x ($x \sim 1.85$)/ SiO_y ($y \sim 0.5$) bilayer nanomembranes as anodes exhibit a reversible capacity of about 1300 mAh g^{-1} at a current rate of 100 mA g^{-1} , an excellent stability of over 100 cycles, as well as a good rate capability. Even after a deep cycling of 180 cycles at different current densities, the reversible capacity can recover completely to the original value at 100 mA g^{-1} . This excellent performance is due largely to the fast ionic transport, powerful strain accommodation and synergistic effect of oxygen-rich SiO_x layer and silicon-rich SiO_y layer.[4]

Multilayer graphene/ GeO_2 tubular nanostructures

In addition, this strain driven strategy was applied to fabricate a new configuration of multilayer hybrid graphene/ GeO_2 microtubes. Similar to previous methods, GeO_2 thin film was firstly deposited on sacrificial layer coated substrates. Followed by a spin-coating of a layer of graphene sheets, these hybrid nanomembranes self-roll into tubular structures driven by the strain. Atomic force microscopy (AFM) measurements show that the thickness of individual graphene sheets is below 1 nm, and the lateral size is 350 nm, meaning that the as-prepared graphene sheets in colloids are monolayers with a C/O ratio of 2.9 according to the X-ray photoelectron spectroscopy (XPS) survey spectrum. These multilayer graphene/ GeO_2 microtubes exhibit unprecedented cycling performance with a specific capacity of 919 mAh g^{-1} at 0.1 C after 100 cycles with capacity retention over 100%. Even at a higher current density of 1 C, a capacity of 821 mAh g^{-1} is retained after 700 cycles with no capacity loss. The rate capability of the graphene/ GeO_2 is also much better than that of pure GeO_2 , which is attributed to the high conductivity of graphene layers in the hybrid. The combination of highly conductive graphene, hollow nanostructures with large surface area and shortened diffusion pathways, and high-capacity germanium oxide renders this hybrid material a truly durable electrode material for lithium-ion batteries. The strain driven strategy further proves the advance of such top-down engineering of nanomembranes for lithium ion batteries.[5]

Sandwich-stacked SnO_2/Cu hybrid nanosheets

As an extension to rolled-up nanotechnology, we employed this method to fabricate sandwich-stacked SnO_2/Cu hybrid nanosheets as multichannel anodes for lithium-ion batteries with the use of carbon black as inter-sheet spacer. From the cross-sectional profile prepared by focused ion beam (FIB) cutting, it clearly shows that CB as sandwich stuffing is tightly clamped between adjacent nanosheets. XPS analysis was performed to reveal the element stoichiometry of SnO_2 , and the results indicate a nonstoichiometric oxygen deficiency (SnO_{2-x}) and a small amount of Sn^{2+} existed in SnO_2 active layer. The sandwich-stacked SnO_2/Cu hybrid nanosheets exhibit significant improvement in cyclability compared to SnO_2 and SnO_2/Cu hybrid nanosheets. By employing a direct self-

rolling and compressing approach, a much higher effective volume efficiency is achieved as compared to rolled-up hollow tubes. Benefiting from the nanogaps formed between each neighbouring sheet, electron transport and ion diffusion are facilitated and SnO₂/Cu nanosheet overlapping is prevented. As a result, the sandwich-stacked hybrid nanosheets exhibit a high reversible capacity of 764 mAh g⁻¹ at 100 mA g⁻¹ and a stable cycling performance of ~75% capacity retention at 200 mA g⁻¹ after 150 cycles, as well as a superior rate capability of ~470 mAh g⁻¹ at 1 A g⁻¹. The cross-sectional profile of the stacked SnO₂/Cu nanosheets at the 100th fully charged state was examined by FIB cutting, and the results indicate that lithium-driven structural and morphological changes of the sandwich-stacked nanosheet systems are well reserved due to the excellent structural stability. This facile synthesis approach also presents a promising route to design multichannel anodes for high performance Li-ion batteries.[6]

2) Nanomembranes prepared via a combination of the rolled-up nanotechnology and chemical processes

Three-dimensionally “curved” NiO nanomembranes

Combined with rolled-up nanotechnology, three-dimensionally “curved” NiO nanomembranes are developed using thin film deposition followed by a thermal oxidation process. The chemical composition of the product was determined by X-ray powder diffraction (XRD). All the characteristic diffraction peaks can be assigned to NiO in the face-centered cubic phase. The representative high magnification SEM and transmission electron microscopy (TEM) images reveal that the nanomembrane is rolled up around itself, resembling a scroll of parchment with open ends and smooth surface. The corresponding selected area electron diffraction (SAED) pattern indicates the polycrystalline nature of face-centered cubic NiO, which is consistent with the XRD results. From the high-resolution TEM (HR-TEM) measurement, it is observed that the ultrathin nanomembranes are built from numerous NiO nanocrystals around 8 nm in size that are randomly distributed without specific orientations. The curved NiO nanomembranes exhibit both superior power rate and ultralong cycle life when utilized as the anode material for LIBs. The electrodes deliver a high capacity of 721 mAh g⁻¹ at 1.5 C (1 C = 718 mA g⁻¹) after 1400 cycles. Notably, even after cycling at an extremely high C-rate of 50 C (i.e., current density of 35 400 mA g⁻¹), the capacity is able to recover to the initial value when the current rate is set back to 0.2 C after 110 cycles. To the best of our knowledge, such high power rates and ultralong lifespans for nickel-oxide-based electrodes have not been reported previously. Our demonstration with tubular and strain-relaxed structures fabricated by rolled-up nanotechnology is liable to improve the materials tolerance against stress cracking and is therefore promising candidates for increasing the stability of energy storage devices such as lithium ion batteries. More importantly, the process for rolled-up nanomembranes is compatible to industrial-level technologies like e-beam evaporation, sputtering deposition and atomic layer deposition, etc.[7]

Free-standing Fe₂O₃ nanomembranes with ultra-long cycling life

With Fe₂O₃ as a proof-of-concept, free-standing nanomembrane structure is demonstrated to be highly advantageous to improve the performance of Li-ion batteries. The free-standing Fe₂O₃ nanomembranes are fabricated by a peel-off strategy with Al₂O₃ film as sacrificial layer together with thermal treatment. After the e-beam deposition of Fe thin film, the sacrificial layer is selectively etched away and thus collected Fe nanomembranes are annealed in a muffle furnace with air atmosphere. With this method, the Fe₂O₃ nanomembrane electrodes exhibit ultra-long cycling life at high current rates with satisfactory capacity (808 mAh g⁻¹ after 1000 cycles at 2C, 530 mAh g⁻¹ after 3000 cycles at 6C) as well as repeatable high rate capability up to 50 C. The excellent performance benefits particularly from the unique structural advantages of the nanomembranes. The mechanical feature can buffer the strain of lithiation/delithiation to postpone the pulverization. The two-dimensional transport pathways in between the nanomembranes can promote the pseudo-capacitive type storage. The parallel-laid nanomembranes, which are coated by polymeric gel-like film and SEI layer with the electrolyte in between layers, electrochemically behave like numerous “mini-capacitors” to provide the pseudo-capacitance thus maintain the capacity at high rate.[8]

Micrometre-scale α-Si film anode based on nanostructured Cu foil

Combined with e-beam deposition and anodic oxidation, a feasible design to fabricate micrometer-scale Si films deposited on nanostructured Cu foil was developed, and the resulted electrodes present high areal capacity for Li-ion batteries with excellent cycling performance. In this work, nanostructured copper oxides are prepared by anodic oxidation of Cu foil in alkaline solution. The resultant copper oxide nanofibers function as matrix for thick Si films (1– 2 μm) loading. Metallic Cu nanofibers are obtained by *in-situ* electrochemical reduction at low potentials, which work as electrical highways for fast electron transport and a reliable mechanical matrix to accommodate volume changes during lithium-silicon alloy/dealloy processes. The engineered thick Si film anode exhibit both high areal capacity (0.48 mAh cm⁻² for 1 μm Si film and 0.6 mAh cm⁻² for 2 μm Si film after 200 cycles at 0.225 mA cm⁻²) and excellent rate capability (0.52 mAh cm⁻² at 1.05 mA cm⁻² for 2 μm Si film). The 2 μm silicon film electrode is able to recover to the initial value of 1 mAh cm⁻² when the current rate is set back to 0.15 mA cm⁻² even after cycling at high current rates. The reported concept can be a general method for high-loading-film electrodes, which is industrial scalable and compatible with current battery manufacturing processes.[9]

3) Integration of nanomembrane into microscale energy storage devices

Supercapacitors, as a new class of energy storage device, can store high energy and provide high power, bridging the gap between rechargeable batteries and conventional capacitors. The rapid advance of portable consumer electronics

stimulates the development of small, lightweight, flexible, and even wearable micro-scale power sources. Particularly, a fully functionalized microscale energy storage device plays the crucial role for the on-board power supply for autonomous microsystems. Therefore, a new concept was introduced to fabricate on chip, all solid-state and flexible micro-supercapacitors based on MnOx/Au multilayers in our institute. In this work, a symmetrical, all solid-state and flexible micro-supercapacitor, which is integrated on flexible polyethylene terephthalate (PET) substrates, was fabricated. Electron beam evaporation was used to deposit MnOx/Au multilayer thin films as electrodes, in which very thin layers of gold were incorporated into the MnOx layer as conductive additives to enable effective charge transport and electrode integrity, thus endowing the electrodes with high capacity, high rate-capability and excellent cycling stability. A gel solution of polyvinyl alcohol (PVA) mixed with sulfuric acid (H₂SO₄) served as a solid state electrolyte. The as-obtained micro-supercapacitor exhibits a maximum energy density of 1.75 mW h cm⁻³ and a maximum power density of 3.44 W cm⁻³. A volumetric capacitance of 32.8 F cm⁻³ is obtained for MnOx/Au multilayer electrodes at a scan rate of 1 V s⁻¹, which is much higher than the bare MnOx electrode. The MnOx/Au multilayer micro-supercapacitor also shows good long-term cycling stability, with a capacitance retention rate of 74.1% after a large cycling number of 15 000 times. With thin film nanotechnology, we introduced a new concept to fabricate on chip, all solid-state and flexible micro-supercapacitors based on MnOx/Au multilayers, which are compatible with current microelectronics. Furthermore, the nature of the process allows the micro-supercapacitor to be integrated with other micro-devices, to meet the need for microscale energy storage. This synthesis approach presents a promising route to design electrodes with thin film nanotechnology for high performance energy storage devices.[10]

A single rolled-up Si tube battery

As demonstrated in above works, various materials with rolled-up tubular structures for advanced LIB anodes, such as Ge/Ti, C/Si/C, GeO₂, SnO₂/Cu, NiO, Fe₂O₃ and SiO_x/SiO_y, all of which have shown enhanced performance (e.g., capacity and cycling stability) due to the fast ionic transport and powerful strain accommodation benefited from the unique hollow micro-/nanohierarchical structure. In this work, a lab-on-chip electrochemical device based on rolled-up nanotechnology is developed, which allows for a comprehensive understanding of the correlation between the electrodes' tubular structure, electrical/ionic conductivity and the electrochemical kinetics as well as the performance in a single unit of active material (herein a single rolled-up tube). Working as the anode in Li-ion batteries, cyclic voltammetry curves of the Si tube exhibit sharp, better-resolved peaks compared with those of a planar Si film due to the enhanced diffusion effect in the unique tubular structure, which makes the rolled-up tube a promising candidate for an ultramicroelectrode for electrochemical

studies. A maximum electrical conductivity occurs after the lithiation of the Si tube. After three cycles, the tube exhibits a highly wrinkled structure due to the strain-induced local deformation, which could be exploited to maintain a stable charge/discharge cycling. The single rolled-up tube battery developed here is promising for the fundamental research of voltammetry and electrochemical processes, and could also be used as local on-chip energy supply or for driving ultra-compact autonomous microsystems.[11]

3.3 In situ characterization

On the basis of rolled-up nanotechnology, single microtube battery devices are developed, which allows us to *in-situ* probe the direct correlation of electrical transport and electrochemistry properties at a single tube level. By performing lithiation/delithiation with one contact as the anode against Li foil, a conductivity measurement was carried simultaneously via another two contacts on the same device. Transport measurements on single microtubes show that the conductivity of the hybrid Ge/Ti microtube ($2.38 \times 10^{-2} \text{ S cm}^{-1}$) is increased by more than two orders of magnitude over that of the pure Ge microtube ($1.28 \times 10^{-4} \text{ S cm}^{-1}$). The ease of fabrication of single rolled-up microtubes on semiconductor substrates makes them more suitable for lab-on-chip microbattery applications as well as micro-integration with other electronic devices.[2]

3.4 Summary

In summary, we have intensively investigated the nano-scaled structures for electrochemical energy storage in autonomous microsystems within this project. From nanomaterials fabrication to characterization (XRD, AES, XPS, TEM etc.), as well as electrode preparation and electrochemical measurements, all the 5 institutes closely cooperated and fruitful results have been achieved. Based on these results, the underlying working mechanisms and especially degradation phenomena are well analysed. Remarkably, rolled-up nanotechnology, as the core strategy for nanomembranes fabrication in this project, provides a straightforward and novel way to fabricate micro-devices, allowing us to explore the reaction mechanism at micro-level. Combining the knowledge from both optimized nanomaterials and micro-device preparation, we can envision a fully integrated energy storage microsystem in the near future, which could pave the way towards autonomous microsystems for practical applications.

4. Publications

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