Авторска справка на научните приноси във всички трудове

(превод на английски език)

Научни приноси на публикациите включени в докторската дисертация

- The role of the initial redox state of the polymer layer for the electrocrystallization of copper has been studied. It has been established that in a reduced state, corresponding to low electronic conductivity of the polyaniline coating, the initial stage of metal crystallization is highly hindered, while in an oxidized state of the polymer the electrocrystallization process proceeds at significantly lower overvoltages (2001, Electrochem. Commun, 3, 312;).
- 2. The electrocrystallization of copper in reduced polymer layers has been used as an indicator method to reveal the different degree of defectivity of polyaniline layers synthesized by different electrochemical methods. It has been found that layers synthesized by pulse potentiostatic procedure are the most homogeneous and have the lowest number of macrodefects (2001, Electrochem. Commun, 3, 312;).
- 3. Comparative study of chemically and electrochemically synthesized polyaniline layers was performed. It was found that the two types of layers are indistinguishable in terms of their redox behavior and stability but differ in their surface structure. This has a significant impact on the electrocrystallization of copper particles in/on the layers. The looser and coarser structure of the chemically synthesized polyaniline layers facilitates the nucleation and growth of the metal phase (2003, Thin Solid Films, 441, 44).
- 4. Comparative study of copper crystallization in polyaniline layers using oxalate and citrate anion complexes of copper was performed. It is shown that the use of metal anion complexes allows to significantly influence the number, shape and size of the deposited copper particles. It was found that not the stability of the metal anion complex, but the initial oxidation-reduction state of the polymer layer in the corresponding electrolyte is of decisive importance for the conditions of electrocrystallization (2002, J. Appl. Electrochem, 32, 701; 2002, J. Appl. Electrochem., 32, 709).

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- 5. Detailed study of the kinetics of electrocrystallization of silver crystals in oxidized polyaniline layers, has revealed that the thickness of the polymer layer impacts the type of active sites for silver nucleation. The two types of active sites, located on the areas of the electrode substrate not covered by the polymer in thin layers, and on the polymer surface in thick layers, are characterized by different nucleation frequencies (2004, Electrochim. Acta, 49, 913).
 - 6. Comparative study of the electrocrystallization of silver from solutions of silver cation and two silver anion complexes – silver thiosulfate and silver-EDTA complex in electrodriven and electroless mode was performed. It was found that, due to the specific role of EDTA anions for the surface structure of the polyaniline coating, the silver-EDTA complex is particularly suitable for the electroless deposition of a large number of silver crystals with a narrow size distribution, located on the surface of the polyaniline coating (2005, Electrochim. Acta, 50, 5616)
 - 7. The possibility of controlling the amount of the deposited metal phase during electroless deposition on reduced conductive polymer coatings has been for the first time demonstrated. It has been found that factors such as the redox charge of the polymer coating, the concentration of the reducing metal ion, and the immersion time can effectively control the number and size of the deposited metal particles by means of electroless process. (2005, Electrochim. Acta, 50, 5616).

Публикации изисквани за научна степен доцент (Приложение 3, В4 и Приложение 4, Г7, Доцент)

 The structure and electrochemical behavior of thin layers of ordered titanium dioxide nanotubes (TiO₂NT) prepared by anodic oxidation of titanium foil in an ethylene glycolbased electrolyte containing fluoride ions have been studied. The layers were tested as an anode material for lithium-ion intercalation in a standard electrolyte (lithium salt dissolved in organic carbonates, 1 M LiPF₆ EC:DMC) and in an ionic liquid-based electrolyte (1 M LiTFSI, [BMP][TFSI]), which demonstrates low toxicity, low vapor pressure, and high ignition temperature. It was found that the type of electrolyte does

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not affect the voltammetric behavior of the amorphous TiO₂NT layers. This result can be related to the disordered structure of TiO₂ and the larger number of defects characteristic of the amorphous material, providing a large space for Li ion intercalation. In contrast, TiO₂NTs built from crystalline anatase show inhibition of Li intercalation in 1 M Li [TFSI] [BMP][TFSI], expressed by an increase in the overpotential of the process. The observed effect is commented as a result of the joint influence of the high viscosity of the ionic liquid [BMP][TFSI] and the crystalline nature of the material.

In both electrolytes, the amorphous TiO_2NT nanostructures demonstrate high capacity, good current efficiency and high electrochemical stability under repeated galvanostatic cycling. In contrast, a decrease in capacity is observed in the layers of crystalline TiO_2NT , which is attributed to the presence of microstructural defects formed during the annealing of amorphous TiO_2 (2013, Electrochim. Acta, 104, 228-235.).

The ordered structures of TiO₂NT were used as a substrate for magnetron sputtering of Si. The performed optimization of the deposition parameters (power and time) allowed obtaining a specific morphology of Si with sufficient free space, suitable for application as anode material in lithium-ion batteries. The nanostructured Ti/TiO₂NT –Si layers were electrochemically tested in an ionic liquid-based electrolyte (1 M Li [TFSI] [BMP][TFSI]). The results show a promising future for the application of the ionic liquid [BMP][TFSI] as a suitable electrolyte, compatible with silicon anodes, having a positive impact on the environment and offering good safety. It was found that the Si structure obtained at 50 W/454 s on an amorphous TiO₂NT template has excellent electrochemical behavior upon repeated cycling, completing the 200th galvanostatic cycle with a capacity of 1150 mA h g⁻¹. The promising results of this type of structure are associated with the specific morphology of the silicon deposit and the mechanical stability of the amorphous TiO₂NT (2014, J. Electroanal. Chem. 731, 6-13,).

2. Nanoporous Si was prepared by metal-assisted chemical etching (MaCE) of silicon substrates. The method allows for the rapid preparation of thin nanostructured silicon layers with tunable thickness and porosity. The lithiation of these structures was tested by voltammetric and galvanostatic electrochemical cycling in a conventional electrolyte

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(1 M LiPF₆ EC/DMC) and in an ionic liquid-based electrolyte (1 M Li[TFSI], [BMP][TFSI]). The nanostructured silicon has a good electrochemical behavior in 1 M LiPF₆ EC/DMC electrolyte and higher activity compared to the unstructured silicon surface. The evaluation of the charge/discharge capacity of the obtained nanostructures shows a limited contribution of the underlying Si substrate, which in turn is beneficial for the long-term stability of the electrode.

The nanostructured Si, measured in an EC/DMC-based electrolyte, demonstrated a 20% capacity reduction during 30 galvanostatic cycles, reaching stable values of 3900 mAhg⁻¹. In contrast, experiments performed in ionic liquid showed lower capacity and current efficiency. The possible reason for this observation can be summarized as the joint influence of the high viscosity of the ionic liquid, the small pore diameter of the nanostructured layer and the crystalline structure of silicon (2014, J. Appl. Electrochem., 44, 159-168).

3. Sulfur and carbon-doped anatase nanoparticles were synthesized via a one-step method based on the interaction between thiourea and metatitanic acid (2016, Nanoscale Research Letters, 11, 140, 2016,, J. Power Sources, 326, 270-278). Electron microscopy shows randomly distributed micrometric-sized crystalline aggregates consisting of many TiO₂ nanoparticles (TiO₂NPs) with a size of 25–40 nm. XPS confirmed that carbon exists in both elemental and oxide forms, and it is mainly adsorbed on the surface of the particles. The analysis proved the presence of sulfur in the S⁶⁺ sulphate form, without the presence of Ti-S and C-S chemical bonds.

The voltammetric behavior of the titanium dioxide nanoparticles showed a noticeable acceleration of the lithiation/delithiation kinetics of the doped SC-TiO₂NPs material. This effect can be assessed by the high voltammetric current and the reduced overpotential, characteristic of the doped titanium dioxide. The determined by galvanostatic intermittent titration technique (GITT) apparent Li* diffusion coefficient demonstrates increased values for the SC-TiO₂NP nanomaterial, confirming that doping with S and C positively influences the Ionic transport in the nanoparticle structure. The synthesized SC-TiO₂NP nanomaterial has excellent electrochemical behavior in terms of capacity

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(initial values of 210 mAh g-1) and very fast electrochemical kinetics, superior to undoped TiO₂. In addition, SC-TiO₂NP exhibits increased electrochemical stability (83% capacity retention over 500 galvanostatic cycles) and nearly 100% current efficiency. (2016, J. Power Sources, 326, 270-278)

4. Thin composite films containing silicon, electrochemically deposited on copper substrates at a constant potential in an ionic liquid electrolyte (1 M SiCl₄ [BMP][TFSI]) were studied. The electrochemical quartz microbalance (EQCM) measurements revealed a significant contribution of side reactions taking place in parallel with the Si electroreduction process. The performed XPS analysis of the elemental composition and chemical structure of the deposited films shows a main contribution of Si, C and O during the electrodeposition process, while N and F are present in lower amounts. The absence of [TFSI] related components in the C1s and N1s spectra is a sign of the fragmentation of [TFSI] on the electrode surface, which allows the incorporation of oxygen, carbon, nitrogen and fluorine atoms into the growing layer, while [BMP]* cations are more stable and remain accumulated on the surface. The electrodeposited siliconcontaining layers demonstrate stable galvanostatic behavior, reaching capacity values of about 1200 mAh g1 and 80% capacity retention after 300 electrochemical cycles in a standard electrolyte. In contrast, in an ionic liquid environment the material has a lower capacity (about 500 mAh g⁻¹). The effective preservation of the structural integrity of the layer during electrochemical cycling and the good electrochemical behavior can be attributed to the incorporation of organic by-products of the ionic liquid decomposition, acting as a buffer against the accumulation of mechanical stress during the lithiation process (2015, Electrochim. Acta 168, 403-413). The effects of viscoelasticity and surface roughness of silicon-containing layers were investigated by analyzing the acoustic impedance of the growing layer. The results were evaluated using theoretical models for the interpretation of acoustic impedance of a viscoelastic layer, and a model accounting for the effect of surface roughness. The performed analysis showed a change in the influence of viscoelasticity and morphology with deposition time. While in the early stages of deposition the viscoelastic properties of the layer determine the

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acoustic impedance, in advanced times the development of uneven morphology of the layer shows a greater impact (2016, Electrochim. Acta 219, 251-257).

- 5. The electrochemical behavior of SnO₂ nanoparticles obtained by electrooxidation of tin using a pulsed alternating current technique was investigated. The electrode material was tested as an anode for lithium-ion batteries and demonstrated promising results, with the initial capacity at the first galvanostatic cycle being about 680 mAh g⁻¹, almost reaching the theoretical possible capacity of the material (2016, J. App. Electrochem. 46, 527-538). The pulsed electrochemical technique based on alternating current has also been used to prepare hybrid MO_x–C (M = Sn, Ni) supports and Pt/MO_x –C catalysts for application in direct alcohol fuel cells. The Pt catalyst on the SnO₂–C hybrid support has good electrochemical stability in acidic solution, and Pt/NiO–C in alkaline electrolyte, respectively. The proposed method provides several advantages over a number of other preparation methods, such as the fact that it is not multi-step and complex, and takes a short preparation time. Furthermore, it eliminates the use of corrosive reagents, toxic organic solvents, and the need for a calcination step at high temperatures (2016, J. Appl. Electrochem. 46, 245–1260).
- 6. The self-combustion synthesis method was applied to prepare Al- and Fe-double substituted cathode material with the stoichiometry LiNi_{0.6}Mn_{0.2}Co_{0.15}Al_{0.025}Fe_{0.025}O₂ (NMCAF). The new NMCAF material showed improved capacity and high stability during galvanostatic cycling. Structural characterization by means of XRD demonstrated that NMCAF crystallizes in an α-NaFeO₂-type structure. The lattice parameters a and c are larger for NMCAF (2.868 Å and 14.211 Å, respectively) than for the unsubstituted material NMC-(3:1:1), 2.861 Å and 14.167 Å, respectively) due to the cationic substitution of Co³⁺ with Fe³⁺. Electron paramagnetic resonance (EPR) showed a redistribution of Ni ions in the structure after replacing part of Co with Al and F, which may be the reason for the reduced cation mixing in NMCAF. It was found that the reduction of the undesirable effect of cation mixing in NMCAF stabilizes the material structure and improves its electrochemical behavior (2014, J. Power Sources, 268, 414-422).

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A thin-film calorimeter has been developed to study the thermodynamic 7. properties of thin films, including energy storage materials. The new method is based on high-temperature stable piezoelectric resonator working as a highly sensitive planar temperature sensor. For the purpose of the study, thin films of the material of interest are deposited on the resonators. The generation or absorption of heat by the active layer during a phase transition leads to temperature changes that can be easily observed insitu by changes in the resonance frequency. This allows the temperature and time dependences of the phase transformations to be analysed, as well as the associated enthalpies to be determined. To cover the temperature range from -20 to 1000 °C, hightemperature stable piezoelectric langasite (La3Ga5SiO14) resonators are applied. The developed method has been applied to study the thermodynamic parameters of various energy storage materials used in lithium-ion batteries. The melting and other phase transition temperatures, as well as the associated enthalpies, are important for the development of advanced materials in this field. A number of active materials (NCA, LMO and MoS₂) as well as a solid electrolyte (LVSO) suitable for solid-state lithium-ion batteries have been studied using this method (2015, J. Electrochem. Soc. 162, A727-A736, 2013, J. Mater. Sci. 48, 6585-6596, 2017, Int. J. Mater. Res. 108, 904-019, 2013, J. Appl. Electrochem. 43, 559 - 565).

8. The electrochemical in-situ dilatometry was applied to study the intercalation-induced macroscopic expansion of electrodes for lithium-ion batteries. The method can be used to study expansion under real conditions. It allows in-situ measurement of the expansion of both novel and conventional electrodes/active materials, separators and electrolytes. Additionally, a theoretical approach has been developed to estimate the reversible expansion of the electrode using a small number of material-specific initial parameters. Furthermore, electrochemical in-situ dilatometry is able to detect the irreversible expansion of materials depending on a number of parameters and is therefore a powerful technique for assessing their stability in real applications. The capabilities of the method have been demonstrated for dilatometric in-situ analysis of a LiNi_{1/3} Mn_{1/3} Co_{1/3} O₂ (NMC) – graphite galvanic cell (2017, J. Power Sources, 342, 939-946).

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An electrochemical-mechanical model of a lithium-ion cell at the macroscopic level is created and implemented. The model is based on the effects of electrode expansion, stress generation and ion transport in the porous electrodes and the separator. In this theoretical approach, the fundamentals of electrochemical processes follow the Newman model, and electrode expansion is implemented according to [2017, J. Power Sources, 342, 939-946,]. For the first time, the physical principles of pore structure compression are directly linked to the electrochemical model of electrode processes in the cell. The experimental parameterization focuses on the pressure-dependent electrolyte transport in the electrodes and the separator. This can be achieved by determining the resistance in the porous structures, carried out in symmetric cells by impedance spectroscopy and compressibility measurements. The developed model has been validated and applied to assess the consequences of elevated pressure conditions (2018, J. Power Sources, 378, 235-247).

- 9. A conductometric technique is proposed for electrocatalytic chemical sensors based on conductive polymers. The lateral conductivity of the polymer layers is measured by two- and four-point techniques. The approach is applied to the electroanalytical detection of ascorbic acid on electrocatalytically active polyaniline and poly-orthomethoxyaniline electrodes. Both polymers show a monotonic dependence of the conductivity on the concentration in the analytically important submillimolar concentration range of ascorbic acid. The method is tested in model solutions of ascorbic acid in buffer and is applied for the detection of ascorbic acid in orange juice (2006, Electrochem. Commun., 8 (4), 643-646).
- 10. The electrochemical formation of TiO₂-polyaniline (PANI) composite layers was carried out by anodic polymerization of aniline in the presence of TiO₂ nanoparticles. The electrochemical, photoelectrochemical and morphological characteristics of the composite layers were studied. It was found that thick composite layers do not show a photoresponse, while thin layers prepared by several potentiodynamic scans had small photocurrents, almost independent of the layer thickness. Due to the small photocurrents of the composite single layers, bilayer structures consisting of a first primary PANI layer followed by an outer TiO₂-PANI composite layer were also

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investigated. It was found that the bilayer structures had up to three times larger photocurrents than the composite single layers. The TiO₂-PANI composite layers were further modified by depositing platinum particles using galvanostatic electroreduction or photoreduction in the presence of hexachloroplatinate anions (2008, J. App. Electrochem. 38, 63-69).

- 11. Multilayer structures of conducting polymers were fabricated by a simple automated adsorption in flow mode. Polyaniline and poly(styrene sulfonate) were used as a model system, allowing rapid electrochemical and spectroscopic determination of the amount of deposited material. The technology was applied for the layer-by-layer deposition of up to 100 bilayers. The results show a well-reproducible and almost constant amount of adsorbed polymer in each deposition cycle. The method can be applied for the deposition of other conducting or non-conducting polymers, biological macromolecules, and composites of polyelectrolytes and nanoparticles (2009, Macromol. Mater. Eng., 294 (6-7), 441-444).
- 12. Multilayered nanocomposites of polyaniline (PANI) and gold nanoparticles (AuNPs) were formed by layer-by-layer deposition. The formation of PANI-AuNPs multilayer structures was investigated by UV-vis absorption spectroscopy and cyclic voltammetry. Each deposited double layer of PANI-AuNPs led to a monotonic and nearly linear increase in both the optical absorption and the oxidation current of PANI. The prepared multilayer nanocomposites were characterized by in-situ conductivity measurements at different pH and potentials and by transmission electron microscopy. It was found that the protective shell did not hinder the electrochemical activity of AuNPs in the nanocomposite. At the same time, citrate anions introduced into the multilayer structure through the AuNPs adsorption steps provided stable doping of the PANI structure, leading to significant electrochem., 14, 1261-1268).

The studies on the structure of PANI-AuNP deposited by LbL technique were supplemented by elucidating the role of the duration of the adsorption step for the formation of the nanocomposite. Microgravimetric measurements during the adsorption process showed that the total amount of adsorbed material (both PANI and

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AuNP) as well as the relative AuNP content increased with increasing duration of the AuNP adsorption step. It was found that the sensitivity of PANI-AuNP for dopamine oxidation depends on the type of nanocomposite (i.e. different AuNPs adsorption times / AuNPs amounts), while for uric acid oxidation the sensitivity remained unaffected by the type of nanocomposite structure. This result is discussed in terms of the different limitations for the two oxidation reactions. Differential pulse voltammetry experiments have shown linear concentration dependences of the anodic peak currents for both dopamine and uric acid in the concentration ranges 7–148 µmol dm⁻³ and 29–720 µmol dm⁻³, respectively. No interference effects were detected in the presence of either analyte (2011, Electrochim. Acta 56 (10), 3693-3699).

- 13. The layer-by-layer adsorption (LbL) technique was used to deposit a novel electrocatalytic material consisting of palladium nanoparticles (Pd NPs) and polyaniline (PANI). The LbL technique offers a way to increase the active Pd surface area within a three-dimensional nanocomposite structure. It was found that, depending on the concentration of the PANI solution used for adsorption, composites with different conductivity (close to that of polyaniline and close to the metal) can be obtained. The nanocomposites were studied as electrocatalytic materials for hydrazine oxidation. A linear concentration dependence of the voltammetric peak currents was observed in the concentration range of 40–800 μM hydrazine, with the sensitivity increasing with the amount of adsorbed Pd NPs. Amperometric measurements show a linear response in the range 10–300 μM with a sensitivity of 0.5 μA/μmol cm⁻² and a theoretical lowest detection limit estimated at 0.06 μM (2010, Sensors and Actuators B: Chemical 150 (1), 271-278, 2010, Pure App. Chem. 83 (2), 345-358).
- 14. The layer-by-layer (LbL) adsorption technique was used to prepare thin composite layers consisting of polyaniline (PANI) and Pd particles by two different methods: (i) multi-step adsorption of PANI and pre-synthesized Pd nanoparticles (PdNPs) and (ii) multi-step adsorption of PANI and polystyrene sulfonate (PSS) followed by electroless deposition of palladium particles (Pd_{eless}). The formation of both types of composite layers was characterized by electrochemical and microgravimetric measurements.

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Electrochemical measurements for hydrogen peroxide reduction were carried out at neutral pH, under voltammetric and amperometric conditions. It was found that the PANI–Pd NPs composites showed a sensitive voltammetric response for H_2O_2 reduction in the concentration range of 40–300 µM, while the (PANI–PSS)Pd_{eless} composites had a high electroactivity that masked the signal from H_2O_2 . Amperometric data showed high sensitivity of both types of composites: PANI–Pd NPs and (PANI–PSS)Pd_{eless} (2013, Electrochim. Acta 90, 157-165).

Публикации в специализирани научни издания, които не повтарят представените за придобиване на образователната и научна степен "gokmop", и за заемане на академичната длъжност "доцент" (Приложение 6, В4 и Приложение 7, Г7)

 Sulfolane-based electrolyte has been used for the first time for electrochemical deposition of silicon. Electrochemical, microgravimetric and spectroscopic methods were combined to study the process parameters and the properties of the resulting layer. The EQCM results support the applicability of the electrolyte for performing electroreduction of SiCl₄ and deposition of Si. The selected experimental conditions allow the formation of thin Si layers with low roughness and minimal inclusion of organic contaminants (2019, Electrochem. Commun, 103, 37-11).

A comparative study of Si electrodeposition in sulfolane-based and ionic liquid-based electrolytes was conducted. Higher contamination with electrolyte decomposition products was observed in the layers deposited in ionic liquid compared to the layers deposited in sulfolane electrolyte. It was found that the substrate plays an important role in the electroreduction of silicon tetrachloride and significantly affects the properties of the deposit. More efficient electrodeposition is observed on metal electrodes (copper, nickel) in both electrolytes due to the accelerated reaction kinetics on this type of substrate. When using glassy carbon, successful deposition can only be achieved in an ionic liquid, however, still showing high levels of deposit contamination (2020, ACS Appl. Mater. Interfaces 12 (51), 57526-57538).

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- 2. The electrochemical nucleation and growth of silicon on glassy carbon in an ionic liquid ([BMP][TFSI]) has been studied by interpreting potentiostatic current transients. A theoretical model for three-dimensional nucleation, taking into account the propagation and overlap of diffusion zones, has been applied to quantitatively characterize the process. In addition to the established methodology for analyzing current maxima in dimensionless coordinates, an interpretation of the entire nucleation process has been carried out by a nonlinear fitting procedure. The initial stages of Si phase formation demonstrate an instantaneous nucleation process, showing a tendency towards a more progressive mode with a decrease in the applied overpotential (2020, J. Crystal Growth, 531, 125346).
- 3. Electrodeposited silicon-containing layers were tested as anodes for sodium-ion batteries. The layers showed a high specific capacity and a long-term electrochemical stability, retaining a capacity of 540 mAh g⁻¹ for at least 400 galvanostatic cycles at a cycling current j = 150 mA g⁻¹. XPS analysis shows that the reversible electroactivity of the material in the sodium-ion electrolyte is due to the joint contribution of carbon and silicon redox centers. The preserved stable function of the layers can be attributed to their improved mechanical stability and accelerated transport of sodium ions in the porous structure of the anode (2022, Energy Technology 10 (5), 2101164).
- 4. Electrochemically formed porous copper was used as a substrate for electrodeposition of silicon. The modified electrode was tested as a binder-free anode, without conductivity enhancing component. It was observed that the porous copper substrate improves the mechanical and electrochemical stability of the electrodeposited silicon. The best electrochemical properties, i. e. specific capacity during lithiation/delithiation and stability under repeated cycling were observed for silicon deposited from a sulfolane electrolyte on a porous copper substrate. The demonstrated positive effect can be associated with the improved mechanical stability of the active material and the

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accelerated ion transport in the porous structure of the anode (2021, Electrochim. Acta 380, 138216,).

- 5. Nickel microfibers with a rough nanostructured surface were synthesized by a one-step chemical process at temperatures below 100 °C. By applying the same synthesis procedure under the influence of a magnetic field, well-ordered, parallel-oriented nickel microfibers were obtained. The synthesized microstructures were further partially oxidized to obtain hybrid Ni/NiO networks. The temperature conditions during the formation of the NiO phase are important for the electrochemical performance of the binder-free Ni/NiO network anodes. The obtained materials were tested as anodes for lithium-ion batteries. It was found that low synthesis temperatures facilitate the formation of a NiO layer with a reduced number of defects, showing higher reversible capacity and improved stability under repeated galvanostatic cycling (2021, J. Appl. Electrochem., 51, 815-828).
- 6. The analysis of the electrochemical and morphological properties of the lithiumelectrolyte interface plays a central role in the application of metallic Li in safe and efficient electrochemical energy storage. The influence of soluble polysulfides (PS) and lithium nitrate (LiNO₃) on the characteristics of the interface layer (SEI) formed spontaneously on the Li surface before electrochemical cycling was investigated. The evolution of the electrochemical impedance and morphology of the interface as a function of contact time and electrolyte composition was investigated. The main tools used in this study were electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). It was found that the individual addition of polysulfides and LiNO₃ increased the interface resistance, while the simultaneous application of these components was beneficial, reducing the resistive behavior of the SEI. Electrochemical cycling of Li metal in unmodified 1,2dimethoxy ethane (DME)-based electrolyte and tetraethylene glycol dimethyl ether (TEGDME)-based electrolytes resulted in weak morphological changes. In contrast, it

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was found that in the presence of PS and LiNO₃, the interface showed a rough and inhomogeneous morphology (2019, Journal of Chemistry, (1), 4102382,).

- 7. Electrochemical quartz crystal microbalance (EQCM) was used for real-time analysis of the formation of electrode-electrolyte interphase layer (SEI) in electrolytes modified with diphenyl octyl phosphate (DPOP) and vinylene carbonate (VC). Rapid SEI formation was observed in the DPOP-containing electrolyte, while slow growth was observed in VC-modified and reference electrolytes. Dry-state QCM measurements showed a significant mass loss in DPOP and reference samples and a negligible mass loss in SEI formed in the presence of VC. The results showed that VC improved the stability of the SEI, while the addition of DPOP or no addition led to the incorporation of weakly bound particles, leading to layer instability. The apparent increase of the damping, Δw and D, during SEI formation in the presence of DPOP is a signal of pronounced viscoelasticity of the layer (2019, ChemPhysChem, 20 (5), 655-664).
- 8. The Taguchi method (TM) was used to determine the relative influence of the experimental conditions on the intensity of the corrosion process in lithium-ion batteries. Based on the results obtained from the analysis, the properties and structure of the lithium salt have the greatest influence on the corrosion process in lithium-ion batteries. On second place is the temperature, responsible for the kinetics of the process, followed by the composition of the solvent mixture. TM is proposed as an approach to conduct less resource-intensive research in the field of developing electrochemical energy sources and is validated to ensure its reliability (2020, Electrochim. Acta 360, 137011).
- 9. Solid-Electrolyte Interphase (SEI) formation was studied by in-situ electrochemical dilatometry. It was observed that the addition of vinylene carbonate (VC) reduces the irreversible expansion of the graphite anode, while the absence of this additive leads to a large irreversible expansion of the electrode. Impedance analysis reveals that the formation of SEI in the presence of VC limits the ion transport in the porous anode. The

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obtained results are important for the design of high-performance lithium-ion batteries (2020, J. Power Sources 457, 228020).

- 10. The corrosion of lithium in contact with a copper substrate, (Cu-Li), was studied using a combined in situ ZRA (Zero-Resistance-Amperometry)-QCM method. This new technique allows measurement of the gravimetric response due to electrochemical deposition or dissolution in parallel with the galvanic current. In the present case, the galvanic current in the system Cu-Li when immersed in electrolyte was measured using ZRA, and the deposition of reduction decomposition products of the electrolyte on the copper surface was measured using QCM. The process of Cu-Li contact corrosion was studied in a sulfolane-based and conventional Li-ion battery electrolyte, where it was found that an adsorbed layer of polyethylene oxide (PEO) on the copper surface can be applied to inhibit the contact corrosion (2023, Electrochim. Acta 463, 142853,).
- 11. Polyaniline (PANI) layers doped with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) were synthesized in the presence of sulfuric and perchloric acid. The effects of the inorganic acid, the electrochemical synthetic procedure (potentiostatic and potentiodynamic deposition) and the thickness of the polymer layers were studied. It was found that the type of inorganic component present in the polymerization solution has a pronounced effect on the degree of doping in acidic solutions, as well as on the redox activity in neutral solutions. A comparison between potentiostatically and potentiodynamically synthesized layers at pH 7 shows a significantly lower conductivity and a lower degree of redox charge retention in the case of potentiodynamic synthesis. The electrocatalytic activity of the doped PANI for the oxidation of ascorbic acid also depends on the electrodeposition procedure of the polymer, with potentiostatically synthesized layers showing better electrocatalytic activity (2013, Chemical Papers 67, 1002-1011).
- 12. Platinum was deposited on layers of TiO₂ particles formed on Ti substrates (TiO₂/Ti). The deposition process was performed by electroless galvanic exchange of previously deposited copper and subsequent immersion of the Cu/TiO₂ coatings in a chloroplatinic

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acid solution. The spontaneous substitution of Cu by Pt leads to the formation of Pt(Cu)/TiO₂/Ti electrodes. Both platinized and unmodified TiO₂/Ti electrodes were characterized by SEM-EDS, and their electrochemical properties were evaluated by cyclic voltammetry in the dark, and under UV illumination. It was found that while platinized rutile-rich electrodes showed typical Pt surface electrochemistry, anatase-rich electrodes displayed only traces of oxide formation and its reduction. The oxidation of methanol on platinized rutile-rich electrodes proceeds at significant rates and can be further enhanced under UV illumination, as a result of the synergism of Pt and TiO₂ in the photoelectrochemical oxidation of methanol (2012, J. Electrochem. Sci. Eng. 2 (4), 155-169).

Review Articles

- 1. An overview of the different types of charge storage mechanisms present in electrochemical energy storage systems is provided. A clear definition of pseudocapacitance and a quantitative framework for distinguishing it from (diffusion-limited) Faradaic charge storage processes are formulated. A methodology for identification and quantification of Faradaic, pseudocapacitive and capacitive charge storage using conventional electrochemical methods was developed. A description of exemplary electrochemical energy storage systems that combine battery, capacitor and pseudocapacitor features is provided. A detailed guide and easy-to-use scripts for identifying and separating the impact of the different charge storage mechanisms using electrochemical methods are developed (2022, Electrochim. Acta 412, 140072).
- 2. An updated critical review of the main strategies for electrochemical structuring of 3D copper substrates (3D Cu current collectors), methodologies for analysing these structures, and approaches for effective control over their properties is provided. These methods are described in the context of their practical suitability in an attempt to facilitate their easy implementation by research groups and private companies with established traditions in electrochemistry and electroplating. Furthermore, the present review may be useful for specialists with experience in related fields of knowledge such

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as new materials development and surface treatment, where electrochemical methods are often applied. Motivated by the importance of Cu CC applications in energy storage devices, this literature review further discusses the relationship between Cu CC properties and the functional parameters of already implemented electrodes (2023, Energies 16 (13), 4933).

3. This review provides a critical assessment of the mechanisms of aluminum corrosion in lithium-ion batteries, methodologies for analyzing this phenomenon, and approaches for its effective inhibition. Since the influence of multiple factors on the corrosion process has a complex impact, this literature review discusses how they specifically affect the ongoing corrosion. Therefore, appropriate examples of important factors such as electrolyte composition, temperature conditions, and electrochemical parameters are presented to explain the specific mechanism of aluminum corrosion. Since corrosion inhibition is an important technological problem with a huge economic impact, the review summarizes how to achieve this goal by regulating the electrochemical system and enhancing the knowledge for optimal operation of the battery positive electrodes (2021, J. Energy Storage 43).

03.02.2025, Илменау

/Светлозар Иванов /