MULTIFUNCTIONAL COMPOSITE MATERIALS FOR ALTERNATIVE ENERGY STORAGE

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Recent increases in environmental issues are continuing to increase pressure on the world energy infrastructure. Alternative energy storages are under serious consideration. Electrochemical power sources are decided to be more sustainable and more environmentally benign. This work introduces the concept of battery composite materials and their possible design. The paper presents an overview of the research performed at Kyiv National University of Technologies and Design (KNUTD) on battery composite materials. The research areas covered different carbonaceous materials and their composites with polymers, nanoparticles of metal and semimetal, multifunctional catalyst materials, battery architectures and composite material functionalization.

Combinations of two or more different materials are called composite materials. They usually have unique mechanical and physical properties because they combine the best properties of different materials. This study demonstrates the construction of multifunctional composite materials for energy storage devices.

Research methodology

The Department of Electrochemical Power Engineering & Chemistry of KNUTD has all necessary equipment for the R&D of novel materials for batteries, fuel cells, supercapacitors, different electrochemical devises and cells. KNUTD's team has facilities for developing the concept cell of batteries, cell design, technology and troubleshooting, cell optimization studies, cell failure analysis including investigations with internal and external reference electrodes. In addition, a set of analytical and physical-chemical techniques for analysis and preparation of electrode materials for different power sources is available. The main equipment at our disposal is as follows:

SOLAAR S4 Double Beam Automatic Atomic Absorption Spectrometer (from ThermoElectron Co., USA); XRF analyzer X-Supreme8000 (from Cambridge, UK); Argon Glove box UNILAB (from MBraun Inc., USA); Three automatic battery 32-channel battery test systems (from Latvia and Ukraine); Automatic battery ARBIN 32-channel battery test system (from Arbin Instruments Co., Texas, USA); VMP3 automatic multi-channel potentiostat/galvanostat with electrochemical impedance spectroscopy (from Princeton Applied Research, UK); Rotating disc electrode devices EM-04 and VED-06 (from St. Petersburg, Russia); Different technological equipment for coin batteries producing (sizes of 2016, 2325, etc.); General laboratory equipment for synthesis of composite materials (two chemical reactors for synthesis and purifications of different materials and composites from Simax Co., Czech Republic; two furnaces with temperature and gas control, high-speed mixer with viscosity control, etc.).

Results and Discussion

Advanced polymer materials for Li-Ion Batteries

Composite materials for energy storage usually consist of active materials and polymer binders. The active materials are tightly bound to the current collector. For example, the most widely used type of composite material for lithium-ion batteries (LIB) is polymer matrix composites based on polyvinylidene fluoride (PVDF). The developments proposed by KNUTD are extremely interconnected with the radical improvement of LIB performances. This task requires the development and integration of new separators, binders, additives and optimized electrode formulations. The focus of KNUTD is on the development of advanced composite materials based on advanced polymer binders with active materials of LIBs. The activity of KNUTD in this research area is dedicated to binders and conductive additives in both anode and cathode in order to understand how and why these materials work (or do not work). New science-based electrode processing technologies were developed and optimized. Much of the work in this research area is devoted to the evaluation of the materials, electrodes, and cells that were produced. KNUTD is using their capabilities and facilities such as prototype scale mixers, coaters, dryers, filling, and electrode formation. In addition, KNUTD is applying microscopic and spectroscopic tools for studying the chemical, physical, and structural properties of materials, both in the bulk and at the electrolyte/electrode interfaces. KNUTD pays especial attention to optimization of the processing parameters of active components such as mass loading and the thickness of electrode layers.

KNUTD elaborates advanced polymers materials in composites. KNUTD fabricated more environmentally friendly, safer and better performing LIBs. This was achieved by using new low-cost processing methods in which it is possible to tailor different properties of the materials.

Fluoropolymers are the most appropriate choice in terms of thermal and fire resistance, electrochemical stability and electrolytes compatibility. In particular, polyvinylidene fluoride (PVDF) has already been largely and successfully investigated for LIB. The PVDF backbone is modified with co-monomers, to increase the adhesion of binders. Advanced fluorinated polymers were combined to active materials based on aqueous formulations as well. This brings the advantage of a partial removal of the organic solvents from the production of the LIB's electrodes. Different components were tested in various combinations to obtain optimised cells, whose performances are tested.

Sodium carboxymethyl cellulose (CMC-Na, CMC) and PVDF aqueous dispersions have been successfully studied as advanced binder materials for graphite-based negative electrodes and high voltage cathode materials contributing to the optimization of the electrodes formulations. These newly developed binders offer an enhanced cohesion of the electrode particles and improved adhesion to the metallic current collector, leading thereby to an improved electrical contact and electrochemical performance of LIB.

Carbon-based hybrid materials for lithium batteries

In this project, the main tasks of KNUTD were:

(I) testing different solid materials developed for their use as different components of LIB; (II) synthesis and characterisation of carbon-based hybrid materials and (III) selection of different nanostructured graphitisable carbon materials with different structural properties. Especially, KNUTD concentrates on the electrochemical characterization of C/C and C/metal composites.

With these requirements, different synthetic solid materials were developed for their use as different components of the battery. Textural, chemical and structural properties were characterized using different methods. Especial attention was focused on synthesis of silicon multiphase composite compounds. KNUTD research group has studied the effect of dispersion of the ultra-fine silicon, and possibly tin and antimony within a graphite matrix, followed by the surface coating of the matrix by carbon. This approach provides an effective way to develop novel nano-structured anode materials with stable charge/discharge behavior and high capacity (over 1000 mAh/g).

Also, KNUTD focuses on low-cost fabrication techniques for preparation of a cathode with improved characteristics to be used in high-energy-density LIBs. KNUTD has studied the effect of the type and concentration of electron-conducting and ion-conducting fillers, which in addition function as polymer binders on the structure and electrochemical performance of composite electrode materials. The preparation of the advanced composites was carried out either by a one-step low-cost deposition process, or by combining this with conventional `doctor-blade` and casting techniques.

Synthesis and characterization of Pt-free oxygen catalysts

The main task was to develop composite materials for the Ultra High-Energy Li-Air batteries with a specific energy of 500Wh/kg and specific power of 200 W/kg. KNUTD activity fully addresses creating innovative materials and technologies for battery components, material architectures and systems of electrochemical storage within a responsible, sustainable and environmental-friendly approach looking at the entire life cycle.

Various simple metal oxides, perovskites and spinels were investigated as inorganic catalytic active materials. The perovskite oxides have a general formula ABO_3, in which A is the larger cation and B is the smaller one. In the framework of this project, the performance of carbon supported perovskites (such as LaMO3 where M = Fe, Co, Ni, Mn) was tested. The metal oxides having the composition AB_2O_4 are called spinels. Spinels (such as Co_3O_4, $NiCo_2O_4$, $CoFe_2O_4$, and $MnCo_2O_4$) were also investigated for oxygen reduction. Pt-free oxygen catalysts based on transition metal oxides were deposited, chemically and/or electrochemically as ultra-thin films on flat and nanostructured carbons. These materials were studied by KNUTD as a function of composition, deposition conditions and post-deposition heat treatment. Thus, a new non-noble electrocatalysts were prepared and tested for the electroreduction of oxygen (ORR). The catalyst exhibited comparatively good activity for the ORR in both aqueous solution and aprotic electrolytes as well.

Composite materials for lithium-ion capacitor

KNUTD succeeded in building a sustainable and safe hybrid supercapacitor with high specific energy, maintained high specific power and long cycle life. The research program focused on the development of individual cell components such as new electrodes with special attention to the lowest environmental impact and low cost. Subsequently, these components were combined in lithium-ion capacitor.

The efforts on the electrode development are highly critical since the process of electrode development drastically impacts the performance of the final device. Best performing activated carbon and graphite was selected after several material screenings in lab cells. In further attempts to find an eco-friendly solvent for electrode fabrication process, instead of commonly used N-Methyl-2-pyrrolidone (NMP), water-based binders were introduced in the electrode slurry to reduce the production cost and environmental impact of lithium-ion capacitors. Despite the challenging electrode preparation step, Solvay aqueous PVDF dispersions were successfully implemented as alternative binders. In order to boost the specific capacitance and power density of hybrid supercapacitor, Li-based positive electrode materials were blended with activated-carbon electrodes so as to manufacture hybrid type positive electrodes. The best performing cathode was obtained by combining the mixture of lithium iron phosphate (LFP) with activated carbon (AC). For the negative electrode side, carbon-based materials such as graphite, hard carbon or lithium titanium oxide (LTO) were used. Electrodes with high homogeneity, reproducibility, free of defects with perfect adhesion to the current collector were accomplished. After the selection of the cell components and cell configuration, different types of hybrid capacitors were designed and tested in lab cells. Good cycling stabilities of lab-designed cells were also demonstrated with more than 90% of stable initial capacitance after ~10000 cycles at a current density of 20C (Charge time: ~3 min) and a Coulombic efficiency close to 100%. It is estimated that the prototype specific energy could be raised to 100 Wh/kg based on the active material excluding the packaging of the cell.

Conclusions

New composite materials were developed and optimized. Much of the work in this research area was dedicated to binders and conductive additives in both anode and cathode electrodes in order to improve electrochemical performance of alternative energy storages. Much of the work was focused on the production cost and environmental impact. Despite the challenging electrode preparation step, aqueous polymer dispersions were successfully implemented as alternative binders for lithium-ion batteries and supercapacitors. High capacity Li anode materials were developed based on the combination of carbons and semi-conductors and their oxides. KNUTD research develops an effective method of dispersion of the ultra-fine silicon, and possibly tin and antimony within a graphite matrix, followed by the surface coating of the matrix by carbon. According to recent data obtained by KNUTD group, this approach provides an effective way of developing novel nano-structured anode materials with stable charge/discharge behavior and high capacity (over 1000 mAh/g).

Composite materials for the Ultra High-Energy Li-Air batteries were proposed based on various simple metal oxides. Perovskites and spinels were investigated as inorganic catalytic active materials.

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