

# Innovative Materials for Post Lithium-ion Batteries

In this work, an innovative application of cyclodextrin-based nanosponges (NS) as eco-friendly and low cost material for application in energy storage field is introduced. Cyclodextrins are cyclic oligosaccharides composed of glucopyranose units linked through  $\alpha$ -1,4 glycosidic bonds which are produced from starch by enzymatic conversion. Nanosponges are polymerized cyclodextrin by different cross-linkers.

- In Lithium-Air batteries nanosponges were applied to overcome two problems. The conventional synthesis of NS shows very interesting results for application as Oxygen-selective membrane. The CTR-NS@PVdF membrane demonstrates high oxygen selectivity, which increased more than six times respect to PVdF and very low water permeability that reduce almost 98%. The same nanosponge in PEEK polymer matrix NS@PWC with oxygen blocking property was used as lithium-protection membrane.
- A lithium-alternative anode was prepared with embedding of silicon nanoparticles in NS. The pyrolysis of Si@NS provides different silicon mass-loading active material. A passivated silicon with controlled 3% oxide layer creates an intimate contact with nanosponges which buffers the volume change of silicon during cycling. To increase the electric conductivity, the later was wrapped with the reduced graphene oxide. The final anode (Si3@CNS-rGO) provides a stable capacity 1500 mAh/g over 50 cycles. The modified electrode fabrication method and the use of Sodium Alginate binder resulted in preparation electrodes having mechanical properties with a reproducible electrochemical performance. The substitution of the standard electrolyte (EC:DMC (v:v) + 1MLiPF6 + 1% VC) with modified electrolyte EC:DMC (v:v) + LiTFSI + 1% FEC enhanced the specific capacity of the cell.
- In lithium-sulfur batteries, hierarchical carbon (HC-CNS) prepared by pyrolysis of PMDA-NS was applied as conductive matrix for lithium-sulfur cathode. In HC-CNS, mesopores function as electrolyte reservoir and micropores are supposed to be electrochemical reaction's sites. This carbon has possibility to host three times its mass elemental sulfur.
- Electrolyte for lithium-sulfur battery was another subject which is discussed in this thesis. Pyrrolidinium-based ionic liquids were synthesized solvent-free method and used as additive in organic solvent electrolyte. The electrolyte with 20% ionic liquid demonstrates highest capacity while the 10% additive showed a better ionic conductivity. The low lithium polysulfide solubility of ionic liquids, enhanced the specific capacity and coulombic efficiency of lithium-sulfur cell. The incompatibility of polymeric separator with ionic liquid was an issue that tackled by the use of fiberglass separator. The best result in terms of capacity and stability was obtained with the use of standard electrolyte and 20% ionic liquid (STD+20%IL) with both separators.

- A full sulfur cell with silicon-based anode and sulfur cathode synthesized by nanosponge-based material was prepared. The pre-lithiation of anode was performed in EL-cell and this configuration Si@CNS/ DME: DIOX (1:1) + 1M LiTFSI + 0.25 M LiNO<sub>3</sub>/S@HC-CNS was used for CR2032 coin cell assembly. The preliminary results showed that pre-lithiation has crucial effect on the performance of the cell.