Materials for high energy Li-ion and post Li-ion batteries

Daniele Versaci

* * * * * *

Supervisors
Prof. S. Bodoardo
Prof. C. Francia

Doctoral Examination Committee:
Prof. Diana Golodnisky, Referee, University of Tel Aviv
Prof. Catia Arbizzani, Referee, University of Bologna
Prof. Arnaldo Visintin, Referee, University of La Plata
Prof. Barbara Onida, Referee, Politecnico of Torino
Prof. Marco Sangermano, Referee, Politecnico of Torino

Politecnico di Torino
March 5, 2021

Lithium-ion batteries (LIBs) are well established energy storage devices for electronic, transportation and renewable-energy applications.

Nevertheless, to meet the ever-increasing energy storage demand for electrical mobility and smart grid, future batteries have to guarantee higher energy density and, at the same time, sustainable and cheaper solutions.

It is worth noting that, to increase the specific energy of a battery, two possible solutions can be adopted. The first option is related to the increment of operating voltage, adopting the so-called high voltage materials. In this case, together with a higher energy it is also observed an important reduction of the cell safety, due to the well-known instability of liquid electrolytes at high voltage. The second option, investigated in the present work, is the use of electrode materials with higher specific capacity.

In the first part of my dissertation lithium-sulphur system was selected as promising post-lithium ion technology, for high energy application.

Lithium-sulphur (Li-S) technology presents high theoretical energy density (about 2600 Wh kg^{-1}) and low-cost (as sulphur is relatively inexpensive, highly available and non-toxic). Besides these well-known advantages, Li-S systems suffer from some issues, related to the multistep reaction process. In addition to low electronic conductivity of sulphur and Li_2S, and the volume expansion due to the solid-liquid transition during the conversion reaction with lithium, this system is deeply affected by shuttle phenomenon. The so-called "*shuttle effect*" is due to the long-chain polysulfides, which are formed during the first part of the reaction pathway and can migrate from the cathode to the anode side, where they directly interact with metallic lithium by parasitic reaction originating a fast capacity fading of the system.

In this work, the use of a double-layer, based on carbon nitride, is proposed to limit the shuttle effect. Carbon nitride was chosen because it is a non-toxic, cheap and stable material, but in particular because, according to DFT calculation, it can directly interact with long chain polysulfides by electrostatic interaction. The double-layer approach was chosen in order to avoid the direct mixing of carbon nitride inside the slurry composition of the cathode, so guaranteeing a good dispersion of carbon nitride on the electrode surface. Starting from these considerations, carbon nitride was synthetized from different precursors, with the aim of evaluating the polysulfides trapping ability in relation with morphology and surface chemistry of different carbon nitride materials. Carbon nitride was synthetized by a simple thermal condensation route. For the electrochemical characterization, a standard sulphur cathode, simply mixed with Ketjen black, was selected as already optimized in previous works. Melt infusion and/or other more

complex synthesis route could be avoided and the role of carbon nitride-based double-layer could be isolated and properly studied. According to structural, morphological and electrochemical results obtained, carbon nitride synthetized from urea presented the best performances in comparison to carbon nitrides synthesized from dicyandiamide and melamine. The double-layer electrodes showed better electrochemical results than single-layer electrode.

Starting from these first conclusions, a systematic study of carbon nitride was performed in order to study the influence of morphology, structure, amount of additive, *etc*. Therefore, C_3N_4 was synthetized from urea at different temperatures in order to discriminate the influence of the morphology on C_3N_4 role in the polysulfides trapping action. Carbon nitride synthetized at different temperatures showed different specific surface area and different surface functionalities. In particular, the samples obtained at 450, 550 and 650 °C showed a different amount of pyridinic nitrogen, which was demonstrated to directly interact with polysulfides. In conclusion, carbon nitride obtained from urea at 550 °C resulted to be the best candidate as trapping agent in the double-layer sulphur cathode. Lastly, the double-layer was optimized in order to reduce the polarization effect due to a thick second layer. The sulphur/carbon nitride ratio was also optimized: the electrode containing a lower amount of sulphur and a higher S/C_3N_4 ratio demonstrated long cycling performances, for more than 500 cycles, as well as better electrochemical performances at higher C-rates.

Concerning the anode electrode, tin-based materials, especially tin oxide, have been widely investigated as potential graphite-substitute for Li-ion batteries. In comparison to graphite, SnO_2 anodes shows higher theoretical capacity of 1494 mAh g^{-1} vs. 375 mAh g^{-1}. Furthermore, SnO_2 is also easy to produce, inexpensive and environmentally friendly. Unfortunately, during the lithiation process (*i.e.* conversion and alloying reaction) tin oxide suffers from a drastic volumetric expansion that induces surface cracking together with an electrical contact loss with the current collector and subsequent capacity fading.

In this work, two different strategies were presented in order to limit the rapid capacity fading of tin oxide anode, increasing the reversibility of the conversion reaction and at the same time containing the huge volume expansion.

The first strategy reported was a simple and scalable wet impregnation synthesis, where tin oxide was directly grown on the surface of a commercial carbon black (C45). The final hybrid compound, containing a particularly high amount of active material (30 wt.% of SnO_2), showed a specific capacity higher than 600 mAh g^{-1} for 100 cycles and it remained around 500 mAh g^{-1} for more than 500 cycles,

with a coulombic efficiency of about 99.9 %. These outstanding electrochemical results were correlated to an optimal distribution of small tin oxide nanoparticles (average size of 5 nm) directly anchored to C45 surface.

The second strategy adopted g-C_3N_4 as high surface support for tin dioxide growth. In this case, a simple solid-state synthesis was selected, and the tin oxide precursors were directly mixed with an already formed carbon nitride. The final hybrid compound showed a final amount of SnO_2 of about 90 wt.% and a huge specific surface area able to contain the volume expansion of tin oxide particles during the alloying process. The $SnO_2@C_3N_4$ compound showed good electrochemical results, presenting a specific capacity of about 500 mAh g^{-1} for 100 cycles at 1C, and interesting results at higher current regimes.

In conclusion, the double-layer approach, with the addition of carbon nitride obtained from urea at 550 °C, as additive for polysulfides trapping, resulted a valid strategy to increase the electrochemical performances of sulphur-based cathodes.

At the same time both the synthesis approaches used to prepare tin oxide-based materials resulted simple and useful to obtain anodes with improved cycling stability avoiding expensive treatments in order to simplify the process for future optimization and scale-up.
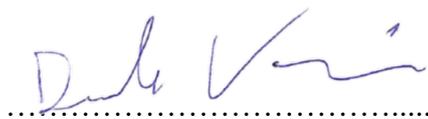
Daniele Versaci
Turin, March 5, 2021