Spinning Disk Reactor technique for the synthesis of nanometric sulfur TiO2 core-shell powder for lithium batteries

Abstract
Sulfur/lithium battery performances are strictly related to morphology and nanostructure of sulfur particles. In this work, a comparison of the morphological characteristics and electrochemical properties of electrodes based on colloidal sulfur obtained by means of traditional chemical precipitation from aqueous solution and via Spinning Disk Reactor (SDR) has been performed. In particular, through SDR technique and by using different fluid dynamic conditions, it is possible to obtain monodisperse and nanometric sulfur particles with higher electrochemical performances when used as cathodic active material in lithium batteries. Moreover, a method to produce core-shell nanoparticles with sulfur and titanium dioxide, starting from a colloidal sulfur (S8) solution produced by Spinning Disk has been performed obtaining good electrochemical results.

Keywords
Lithium battery; Spinning Disk Reactor; S-TiO2.

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Statement Letter of the Article:

“Spinning Disk Reactor technique for the synthesis of nanometric TiO$_2$ sulfur core-shell powder for lithium batteries”

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Dear Editor

It is stated, in this letter, that this work has been presented at the Solid State Ionics Conference in Padua:SSI-21: recent advances in solid state ionics. The code is: I-2_62/P I-2-20170203-161552-9BWW-ORAL. Symposium in Advanced Lithium and Sodium Battery Electrode Materials. Moreover, the submitted paper has not been published previously, is not under consideration for publication elsewhere, and if accepted will not be published elsewhere in the same form, in English or in any other language, without the written consent of the publisher. The authors have no commercial associations or sources of support that might pose a conflict of interest. All authors have made substantive contributions to the study.

Sincerely

Dr. Alessandro Dell’Era
Synthesis of a Colloidal Sulfur solution by Spinning Disk Reactor technique

Synthesis of Sulfur-TiO$_2$ core-shell powder for cathodes in lithium batteries

DLS, SEM, EDX and XRD analyses of Sulfur-TiO$_2$ core-shell cathode

Electrochemical characterization of S-TiO$_2$ core-shell cathode in lithium batteries
Spinning Disk Reactor technique for the synthesis of nanometric sulfur TiO$_2$ core-shell powder for lithium batteries

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Abstract

Sulfur/lithium battery performances are strictly related to morphology and nanostructure of sulfur particles. In this work, a comparison of the morphological characteristics and electrochemical properties of electrodes based on colloidal sulfur obtained by means of traditional chemical precipitation from aqueous solution and via Spinning Disk Reactor (SDR) has been performed. In particular, through SDR technique and by using different fluid dynamic conditions, it is possible to obtain monodisperse and nanometricsulfur particles with higher electrochemical performances when used as cathodic active material in lithium batteries. Moreover, a method to produce core-shell nanoparticles with sulfur and titanium dioxide, starting from a colloidal sulfur (S8) solution produced by Spinning Disk has been performed obtaining good electrochemical results.

Keywords: Lithium battery, Spinning Disk Reactor technique, S-TiO$_2$ core-shell structure.

1 Introduction

Over the years several methods for the production of sulfur nanoparticles have been developed [1-4]; among these, the method of the microemulsion is one of the most important due to its flexibility and the excellent control over the size of the particles [5].

These methods use the same chemical reaction between sodium thiosulfate and hydrochloric acid, but in different fluid dynamic conditions.

In general, the preparation of colloidal sulfur has many advantages such as low cost of reagents, mild temperature conditions and the use of aqueous solutions. The limits of such a procedure are represented
by a poor yield (mass of sulfur on volume of solution) and the difficulty to produce nanometer-size particles. In order to obtain particles under submicron size, particularly dilute solutions have to be used to avoid agglomeration. Chaudhuri et al. [5] have shown that it is possible to get sulfur nanoparticles with an average diameter of about 200 nm by using 5 mM aqueous solution of sodium thiosulfate and a stoichiometric amount of hydrochloric acid.

On the other hand, using different fluid dynamic conditions it is possible to synthesize monodisperse sulfur nanoparticles through the Spinning Disk Reactor (or rotating disk reactor) technique. The Spinning Disk Reactor (SDR) consists of a rotary disc placed horizontally and confined in a cylindrical housing. The reagents, introduced at or near the center of the disc, move quickly pushed outward by centrifugal force. In this way, a thin liquid film is formed on the surface of the disk, exhibiting high micromixing conditions at reduced residence time. In these conditions, the reaction takes place at the nanoscale and the final solution is collected at the basin of the reactor.

Therefore, in particular, in this work we want to emphasize that by using the spinning disk reactor technique under different fluid dynamics conditions, it is possible to obtain a monodisperse and nanometric size sulfur particles having higher electrochemical performance as active material in lithium-ion batteries respect to sulfur particles obtained by colloidal solution.

Another fundamental aspect to take into account is the capacity loss for Li-S cell due to the diffusion of polysulfides in solution. The lithium polysulfides \( \text{LiS}_x \) \( x = 4\; 6\; 8 \) are extremely soluble in traditional electrolytes and their formation, during the cyclation, causes strong morphological and compositional changes inside the cathode.

To overcome this problem, in literature there are two different strategies: (i) prepare composite materials where sulfur is encapsulated in carbonaceous [6-9] and polymer [10] matrix or conductive network of graphite [8], carbon nanotubes [11,12] or graphene [13,14], (ii) synthesize core-shell particles in which sulfur is the core while the shell is often a conductive material or a metal oxide [9,15-19]. For the proper functioning of electrochemical cell, the coating must ensure good electrical conductivity and good ionic and electronic contact.

In this work, a method to produce core-shell nanoparticles with sulfur and titanium dioxide, starting from a colloidal sulfur (S8) solution produced by Spinning Disk Reactor (SDR) and hydrolysis of titanium isopropoxide (TTIP) in a colloidal solution is proposed.
2 Experimental

2.1 Instruments

SEM analysis were obtained by the high-resolution Auriga-Zeiss FE-SEM microscope. The apparatus is also equipped with an EDX detector (Bruker). The size distribution has been measured by Dynamic Light Scattering technique (DLS Malvern, series PCS4700).

The diffraction patterns were obtained by means of diffractometer Rigaku using X monochromatic radiation (Cu-Kα).

The galvanostat used is Maccor Series 4000 placed inside a dry room at controlled humidity (RH < 20 ppm and an average temperature of 21 °C). Data were collected and analyzed through a special interface program (by LabView, 2009). The Spinning Disk Reactor consists of a rotating disc with a diameter of 85 mm, equipped with two injectors placed in correspondence of its center and 10 mm above the surface. The apparatus also includes two peristaltic pumps with variable flow.

2.2 Sulfur synthesis by means of traditional chemical precipitation from aqueous solution

The colloidal sulfur (CS) preparation is obtained by the reaction between sodium thiosulfate and hydrochloric acid in aqueous solution. The reaction can be written as follows:

\[ \text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \rightarrow \text{S} + \text{SO}_2 + 2\text{NaCl} + \text{H}_2\text{O} \]

this procedure has the following advantages:

- The synthesis takes place at room temperature in a single step.
- This process is scalable and uses cheap, non-toxic and easily available materials.
- The particles obtained are compatible with the traditional techniques to produce lithium batteries and enables the use of electrolytes, binder and conductive materials used in industry today.

The concentration of the reactants seems to be one of the most important aspects to control the final size of the particles. In particular, the concentrated solutions of sodium thiosulphate, under normal stirring conditions, cause excessive growth of the particles. On the other hand, excessively dilute solutions do not allow to obtain acceptable yields and make difficult the successive separation step of the material. The colloidal solution has been centrifuged at 4000 rpm for 30 min in order to separate the particles. Finally, to remove the waste products such as NaCl the powder was rinsed in distilled water and centrifuged again. The product was dried under vacuum at room temperature overnight before being used in an electrochemical cell.
2.3 Synthesis by means Spinning Disk Reactor (SDR)

The use of the SDR presents a series of advantages which can be summarized as follows:

• The conditions of micromixing can be obtained within the liquid film over the disc surface by using a low amount of energy
• The reduced residence time and the high local supersaturation values limits the growth after the nucleation allowing the production of nanometric size particles
• The use of concentrated solutions allows to obtain high yields. In addition to this, the synthesis via SDR is a continuous production process that can be easily scaled up for industrial applications.
• The particle size distribution of the product may be controlled by means of the operating parameters such as flow rate of the reactants, rotating velocity of the disc and position of the reactant injectors over the disc surface [20, 21].

For the sulfur nanoparticles synthesis, 200 ml aqueous solution of sodium thiosulfate (Na$_2$S$_2$O$_3$; Aldrich) at 4.3 M concentration have been prepared. Separately, a stoichiometric quantity (1:2 by mol) of hydrochloric acid has been diluted in 200 ml of distilled water. The pump was set to 100 ml/min while the test has been conducted at 1200 rpm disk rate. Once the depletion of the reactants has been reached, the solution has been collected for subsequent centrifugation.

2.4 Core-shell synthesis

The proposed method consists in a TiO$_2$ coating of sulfur particles present in a colloidal suspension produced by a SDR reactor. 50 ml of the colloidal solution were collected and poured into a beaker. Separately, 1 ml of concentrated TTIP (C$_{12}$H$_{28}$O$_4$Ti; Aldrich) was diluted in 20 ml of isopropyl alcohol. The solution was added dropwise to the colloidal suspension previously obtained together with 10 ml of hydrochloric acid (HCl; Carlo Erba) under magnetic stirring. The reaction was allowed to proceed for 2h.

The final suspension was finally centrifuged at 4000 rpm for 30 min. Subsequently, the material was rinsed in distilled water and centrifuged again at 4000 rpm for 15 min. The product was dried under vacuum at room temperature overnight.
3 Results

3.1 DLS analysis
In order to estimate the size of the particles obtained, they were analyzed by DLS (Dynamic Light Scattering). In Figure 1 the analysis results are reported. For CS material (figure 1a), the largest number of particles have an average diameter in the range from 580 nm to 600 nm, while for SDR (figure 1b) the most particles have a diameter in a range from 50 to 70 nm, which means ten times smaller than those produced by simple colloidal solution reaction.

3.2 SEM and XRD characterization
For sample preparation, a drop of highly diluted colloidal sulfur solution synthesized according to (1) has been deposited on an appropriate stub and dried at room temperature over night. Morphological characterization has been performed by FE-SEM analysis.
In Figure 2a it is possible to notice the dispersion and size distribution of particles obtained by CS. The image shows an average diameter of about 1 μm. The observed values are higher than those found by DLS, because Dynamic Light Scattering measurements are carried out in solution, thus preventing the particles agglomeration undergone in the drying process.
Figure 2b shows a detail of the particles in an image with 10000 magnifications. Besides the spherical shape, a characteristic lamellar structure is visible.
In Figure 3, a SEM image of the sulfur particles produced by means of Spinning Disk Reactor is reported. The particles have a spherical shape and the size distribution is in agreement with the results obtained through DLS analysis. In particular, on the picture a diameter of a particle has been reported equal to 82 nm. In Figure 4, instead, two micrographs of the sulfur-titanium dioxide core-shell particles at different magnifications are presented. The core-shell particles have a spherical shape and are sufficiently dispersed. The average size can be estimated by referring to the micrograph in figure 4b.
The image shows an average size of particles produced between 80 and 100 nm. Compared to the method of Cui et al. [15] the used process produces particles, in average, 10 times smaller. In Figure 5 the selected area for the EDX study and the corresponding energy spectra are presented. Both peaks related to sulfur and titanium can be observed, thus confirming the coverage of the particles by TiO₂. However, sodium chloride was also detected.
The sulfur and titanium distribution is represented by EDX maps in Figure 6a) and 6b) respectively. The amount of sulfur into active composite material has been estimated about 20% in weight.
Since the dots referring to titanium are more sparse than those related to sulfur, it is possible to argue that, despite the core-shell configuration obtained, a more homogeneous TiO$_2$ coating is desirable. Figure 7 shows the diffractometric pattern of S-TiO$_2$ sample, which reveals the presence of peaks related to orthorhombic sulfur phase. From the spectrum it is possible to notice that the material is not highly crystalline and some impurities like NaCl are present, but it is also important to highlight that peaks of TiO$_2$ are absent, thus suggesting an amorphous structure.

3.3 Electrochemical characterization

The materials prepared through the colloidal solution, by either CS or SDR technique, have been used for cathodes preparation with addition of Super P carbon and Teflon, using a weight ratio of 40:50:10 respectively. For electrochemical characterizations, a T cell with lithium metal as anode, LTFSI (trifluoromethanesulfonylimide) in DME:DEGDME (dimethoxyethane:diethyleneglycoldimethylether) 1:1 by volume as electrolyte and the material to be tested as cathode, has been assembled. All tests have been performed in a voltage range from 1.6 to 2.8 V and using a constant current. Figure 8-a) shows the discharge curves relative to the first, third, fifth and tenth cycle for a material obtained through CS. It is possible to recognize the typical trend of a Li-S cell with the presence of two distinct plateaus at different potential. The material has an initial capacity of 570 mAh/g, namely about 34% of the sulfur theoretical capacity. This value gradually decreases, reaching 70 mAh/g at the end of the tenth cycle, which means that the electrode loses 82% of its capacity during the first 10 cycles. Figure 9-a) shows the charging curves for the previously mentioned cycle. It can be noted that the capacity value relative to the first cycle is equal to 540 mAh/g, so it is lower than the value obtained during the discharge. This indicates that, once formed, Li$_2$S is not fully oxidized and does not completely participate to the subsequent electrochemical reactions. Furthermore, it is possible that the polysulphides in solution have been reduced chemically to the anode to form a passivating layer on the metallic lithium.

In Figures 8b and 9b, respectively, the curves of discharge and charge sweeps, relative to the first, third, fifth and tenth cycle for a material obtained through SDR are represented. The electrode shows a specific capacity for the first cycle of 1510 mAh/g, which represents 90.4% of theoretical capacity. This value drops to 623 mAh/g during the third cycle to be around 197 mAh/g at the end of the tenth cycle.

The high value of capacity during the first cycle demonstrates the effectiveness of using nanostructured materials for Li-S cell. In order to perform a fair comparison, the electrochemical materials were tested
for 100 cycles under the same conditions. The results obtained are presented in Figure 10a and 10b, respectively, from which it clearly results that the loss of capacity continues even after the tenth cycle for both materials: in detail, the cell passes from 70 mAh/g to 22 mAh/g losing 1.23% of initial value per cycle for the material obtained by CS, and from 197 mAh/g to 70 mAh/g with an average rate of loss equal to 1.53% per cycle for the material obtained by SDR. After the 20th cycle, the capacities are maintained substantially unchanged.

In both cases the loss of capacity in the third discharge sweep is 55% respect to the first one. The decrease of the particle size leads to an increase of the initial capacity equal to more than twice: greater the specific surface, higher the amount of material involved in the lithium sulfides formation process. However, since smaller particle size means higher exposed surface, the dissolution of the high order sulfides [22] in the electrolyte during the cycling is observed as well. The problem may then be solved by producing a core-shell type structure. In fact in this case it is possible to see as the percentage decrease of the capacity of the third discharge sweep, respect to the first one, is only about 7.7 %, although also in this case the capacity tends to decrease for the first 20 cycles and then it stabilizes to a value higher than in the two previous cases. Since EDX analysis suggests that the coating is not homogeneous, it is possible that part of the active material in the poorly covered zones still slowly dissolves, while where the core-shell is well formed there is a good retention of capacity. Moreover, most likely, after the first few cycles, the continuous variations of cathode volume caused the destruction of initial morphology of material. In particular, the strong expansion of elemental sulfur during discharge process also involves the breaking of titanium dioxide rigid shell which surrounds the particles. However, since it forms a mechanical limit to polysulfide mobility, TiO$_2$ can absorb these ions preventing their spread within the electrolyte [23].

In Figure 11 a) and b), the curves for the first, third, fifth and tenth charge and discharge sweep, respectively, are shown for core-shell S-TiO$_2$ materials. With particular reference to the first discharge cycles, the capacity is 1395 mAh/g, namely about 88 % of the sulfur theoretical value. The cell shows a value of 1290 mAh/g and 1270 mAh/g respectively during the third and fifth cycle, and around 1120 mAh/g at the end of tenth cycle. The loss of capacity is 18% of the initial value.

In Figure 12 discharge and charge curves related to thirteenth, seventeenth, fiftieth and hundredth cycle, are shown. It is possible to notice that the capacity measured after 50 cycles is 460 mAh/g, value that remains, as said before, unchanged during subsequent cycles. The trend of capacity as a function of cycle number is presented in Figure 13. The cell, after the twentieth cycle, loses 63% of initial value, even if it maintains a capacity of about 450 mAh/g at the end of the 100th cycles. The results obtained
demonstrate the effectiveness of core-shell configuration in multi-functional design of a sulfur-based cathode. In particular, the high capacity observed during the first few cycles are attributable to the small size of particles which allows an almost total use of active material. Moreover, the presence of TiO$_2$ shell represents a barrier against polysulfides diffusion [15]. Although the material is still unsuitable for commercial battery production, the results obtained represent an important step forward in solving the problems related to loss of capacity in a Li-S cell.

### 4 Conclusions

In this work the electrochemical performances of cathodic electrodes based on monodisperse and nanometric sulfur particles have been analyzed. Generally speaking, regular shape and size allow a wider utilization of the active material which is related to a higher specific capacity. The use of the Spinning Disk Reactor technique allowed us to obtain monodisperse sulfur nanopowders with an average diameter of about 60 nm and to increase the process yield. The comparison between the two different materials investigated highlights as under equal conditions, but using different fluid dynamic regimes, it is possible to control the sulfur particle size. In particular, the nanometric sulfur powder produced by SDR technique shows better characteristics and a capacity, after 100 cycles, more than 3-time superior to the one obtained using material produced by CS, even if both materials have still insufficient performances for battery applications. As far as the core-shell material is concerned, the nanostructured electrode has allowed a wide use of active material and a reduced capacity decay during cycling. In particular, the material showed an initial capacity of 1395 mAh/g equal to 88% of theoretical value. The capacity of electrochemical cell decreases during operation up to 450 mAh/g after about 30 cycles. Then, the material capacity remains unchanged and no substantial loss of capacity has been recorded up to 100$^{th}$ cycle. The results reported prove the effectiveness of core-shell structure for a new multifunctional active material design for Li-S cells.

Despite the problem of loss capacity persists, by means of S-TiO$_2$ core-shell particles, substantial improvements were obtained, which indicates the effectiveness of the proposed strategy. Greater control of TiO$_2$ shell formation and the appropriate engineering of particles with blanks inside, can lead to even better results.
Figure list

Figure 1 a) Particle size distribution of sulfur particles produced by precipitation from colloidal solution (CS)  
b) Particle size distribution of sulfur particles produced by Spinning Disk Reactor (SDR)

Figure 2 a) SEM image of the sulfur particles produced by means colloidal sulfur solution;  
b) particular with 10000 magnification

Figure 3. SEM image of the sulfur particles produced by means of Spinning Disk Reactor

Figure 4 a) A SEM image of S-TiO\textsubscript{2} core shell particles,  
b) a detail of the same image reporting the size of a particle

Figure 5 a) EDX spectra of S-TiO\textsubscript{2} structures related to the selected area in b)

Figure 6 EDX maps for S (a) and Ti (b) for a sample of S-TiO\textsubscript{2}

Figure 7 Diffractometric pattern of S-TiO\textsubscript{2}

Figure 8 a) Discharge curves at C/10 for CS material;  
b) Discharge curves at C/10 for SDR material

Figure 9 a) Charge curves at C/10 for CS material;  
b) Charge curves at C/10 for SDR material

Figure 10 Capacity trend as a function of cycle number a) CS,  
b) SDR

Figure 11 a) Charge curves obtained at C/10 for 1\textsuperscript{st}, 3\textsuperscript{rd}, 5\textsuperscript{th} and 10\textsuperscript{th} cycle  
b) Discharge curves obtained for 1\textsuperscript{st}, 3\textsuperscript{rd}, 5\textsuperscript{th} and 10\textsuperscript{th} cycle

Figure 12 a) Discharge curves obtained at C/10 for 13\textsuperscript{th}, 17\textsuperscript{th}, 50\textsuperscript{th} and 100\textsuperscript{th} cycle  
b) Charge curves obtained for 13\textsuperscript{th}, 17\textsuperscript{th}, 50\textsuperscript{th} and 100\textsuperscript{th} cycle

Figure 13 Capacity trend as a function of cycle number
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