A plasma process in the preparation of Li_2S for lithium-ion battery applications
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Abstract: Plasma technologies are nowadays considered for the development of better performing and more affordable energy storage devices such as the lithium- ion batteries (LIB). Their versatility allows the synthesis of nanostructured electrodes with different morphologies and coatings of carbon or metal oxides, thin films, *etc*. Herein, we highlight the key advantages of their use in LIB technology and we introduce the synthesis of the promising cathode material Li_2S by means of inductively coupled thermal plasma.

Keywords: plasma, lithium- ion batteries, lithium- sulfur batteries, cathode.

1. Introduction

Lithium-ion batteries (LIB) have succeeded as energy storage devices owing to the versatility of their chemistry that allows for an efficient conversion of chemical energy into electrical energy [1, 2]. They have been largely used as power sources in portable electronics and, more recently, in hybrid and electric vehicles as well as in massive storage devices for the grid. In a battery, three key components participate in the energy conversion: one positive electrode (cathode) and one negative electrode (anode) that are separated by an electrolyte. During a typical discharge process, the negative electrode undergoes an oxidation reaction where electrons are removed and flow through the external circuit to the positive electrode to generate the corresponding reduction reaction. The electroneutrality of the electrodes is kept by the transfer of Li^+ through the electrolyte from the negative to the positive electrode.

Most commercially available batteries are constituted of lithium transition metal oxides (*e.g.* $LiCoO_2$) or lithium transition metal polyanions (*e.g.* $LiFePO_4$) for the positive electrode, and of graphite as the negative electrode. $LiCoO_2$ is a layered oxide that intercalates 1 mol of electrons per mol of compound, yielding a theoretical capacity of 274 $mAhg^{-1}$, while $LiFePO_4$ presents an olivine structure with a theoretical capacity of 170 $mAhg^{-1}$. Other compounds have been largely studied such as the spinel $LiMn_2O_4$ which is less toxic and cheaper due to the use of Mn, but which has poorer electrochemical performances caused by parasitic reactions with the electrolyte [3]. More recently, Li-S batteries have attracted great attention since the theoretical capacity of S (1672 $mAhg^{-1}$) and of Li_2S (1166 $mAhg^{-1}$) largely surpass that of $LiFePO_4$ and $LiCoO_2$ and because they are also significantly cheaper [4, 5]. However, difficulties associated with the low conductivity of Li-containing electrodes and with the fast capacity fading are yet to be overcome. In the case of Li_2S, efforts to address the poor electrochemical performance include the formation of carbon coatings on the surface of the particles, polymeric encapsulation, the use of polymeric nanocomposites and porous polysulfide reservoirs [5], among others.

The use of Li_2S presents other challenges regarding its manipulation in air since it is very sensitive to moisture: when in contact with water, H_2S is formed. To date and to the best of our knowledge, there is no common procedure to prepare Li_2S for battery applications and most reports in the literature use commercially available Li_2S as precursors of nano- or microsized Li_2S particles [6–8], mainly due to the fact that the synthesis of lithium sulfide usually involves the use of lithium metal as precursors or the emission of dangerous gases as reaction byproducts. Such is the case of the synthesis of Li_2S using sulfur and triethylborohydride in tetrahydrofurane (THF), where H_2 is produced [4, 9, 10]. Also, Li_2S nanocomposite has been prepared by reacting sulfur/C composite with *n*-butyllithium, which is an air-sensitive compound [11]. Vapor layer deposition has been considered as an alternative approach, where lithium *ter*-butoxide and H_2S (toxic gas) were used as precursors to produced nanosized Li_2S [12]. Moreover, the use of commercial Li_2S is followed by grinding, ball milling or recrystallization in ethanol, which is not efficient in terms of particle size control, crystallinity, purity and costs.

In the search of new methods to prepare nanostructured Li_2S, we propose the use of plasma technologies. It is well known that plasma-based procedures have been developed to synthesize or to modify materials for applications in microelectronics, inorganic nanoparticles and carbonaceous compounds synthesis (*e.g.* graphene, carbon nanotubes), thermal barrier, wear-resistant and corrosion-resistant coatings and solid oxide fuel cells, among others. They are now also considered for the synthesis of nanostructured electrode materials and separators with controlled composition, size and morphology for LIB [13]. Our group recently reported the synthesis of $LiFePO_4$ powders and of binder free coatings by means of inductively coupled thermal plasma using the same precursors used in a conventional synthetic routes (*e.g.* sol-gel) [14]. Although most published studies on plasma-produced electrode materials lack extended electrochemical characterization tests (which usually comprehend cyclic voltammetry, charge-discharge profiles and impedance analysis), great advances have been made in the preparation of nanostructured electrodes with controlled size, morphology and preferred crystal growth, which are critical to shorten Li^+ diffusion paths, increase the electrode/electrolyte contact area and mitigate the volumetric changes of the electrode materials upon cycling. Additionally, the use of plasma technologies often reduces the number of experimental steps required to produce LIB electrodes and almost eliminates the solvent consumption otherwise required to obtain crystallized and purified materials.

Considering the many possibilities foreseen for the preparation of LIB electrode materials by plasma processes and the opportunity our research group sees in contributing to this topic, herein we explore the synthesis of nanostructured Li_2S by means of inductively coupled thermal plasma using a controlled atmosphere reactor adapted with a glovebox and powdered precursors. With this first attempt, we hoped to produce pure Li_2S and to collect it from the reactor in a controlled environment free of moisture. Once the resulting powder was characterized, preliminary electrochemical tests were performed, as reported in this work.

2. Investigating ICP synthesis of Li_2S

2.1. Experimental

The synthesis of Li_2S was performed using an inductively coupled thermal plasma torch (Tekna PL50) equipped with a subsonic nozzle and mounted onto a controlled atmosphere reactor, as illustrated in Figure 1. The reactor pressure was 200 torr, the torch power was 33 kW and the gas flow rates are shown in Table 1. The powdered precursors were axially injected in the plasma at a rate of 1 $gmin^{-1}$. The precursors $LiOH\cdot H_2O$ and S were mixed in stoichiometric ratio, ground for 15 minutes and later placed in a powder feeder that is connected to the injection probe. As sheath gas, a mixture of argon and hydrogen was used while the central gas consisted on pure argon. The use of a reductive plasma flame is key for the reduction of S to S^{2-} and to promote the formation of Li_2S. The plasma reactor used is adapted with a glovebox filled with argon that allows recovering the products of the synthesis in a controlled environment. It is worth noting that all syntheses were carried out using personal protective equipment to prevent contamination when dealing with nanomaterials and possible exposure to highly toxic H_2S.

Table 1. Experimental parameters for the plasma synthesis of Li_2S nanoparticles.

Parameter	**Gas ($Lmin^{-1}$)**
Sheath	Ar (80)
	H_2 (1.7)
Central	Ar (23)
Powder	Ar (20)

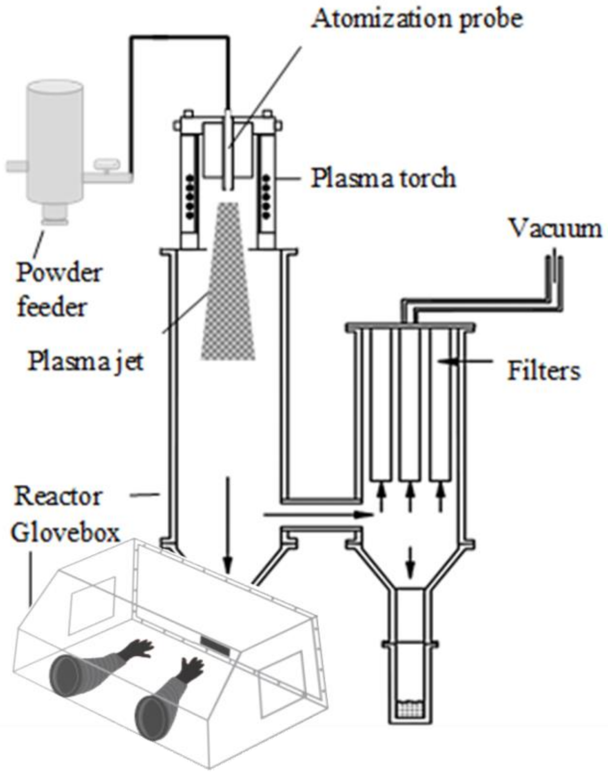

Figure 1. Inductively coupled thermal plasma reactor used for the synthesis of Li_2S powders from powdered precursors. *Glovebox image was taken from www.terrauniversal.com

2.2. Characterization of the plasma- synthesized Li_2S

An X-ray diffraction (XRD) pattern was acquired using a PANalytical X'pert Pro MRD diffractometer while the sample was covered with a Kapton film (PANalytical) to prevent Li_2S decomposition during measurements. Figure 2b depicts the XRD pattern characteristic of Li_2S. Indeed, the main peaks were indexed in the cubic system of space group *F*m3m (PDF: 01-071-4841), allowing to confirm the plasma synthesis of Li_2S. Small amount of impurities were found to consist of LiOH and S, most likely formed due to the decomposition of Li_2S when exposed to air. The morphology of the plasma-produced powder was observed by SEM and was found to consist of agglomerates of spherical particles of tens of nanometers, as illustrated in Figure 2a. Better image acquisition was prevented due to the high insulating character of Li_2S that increases the brilliance when the beam hits the sample and decreases the quality of the images.

In order to test the electrochemical performance of plasma-produced Li_2S, the electrode was prepared inside a glovebox by mixing 50% of plasma-produced Li_2S, 40% of carbon black and 10% of PDVF with N-Methyl-2-pyrrolidone to prepare a slurry. Subsequently, the slurry was casted on an Al foil and dried at 70°C, also in a controlled atmosphere. A 1 cm^2 disk containing 0.9 mg of Li_2S was cut and assembled to a coin cell using 1.0 M of lithium bis(trifluoromethanesulfonyl)imide in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v) as the electrolyte (without additives), and Li metal as negative electrode.

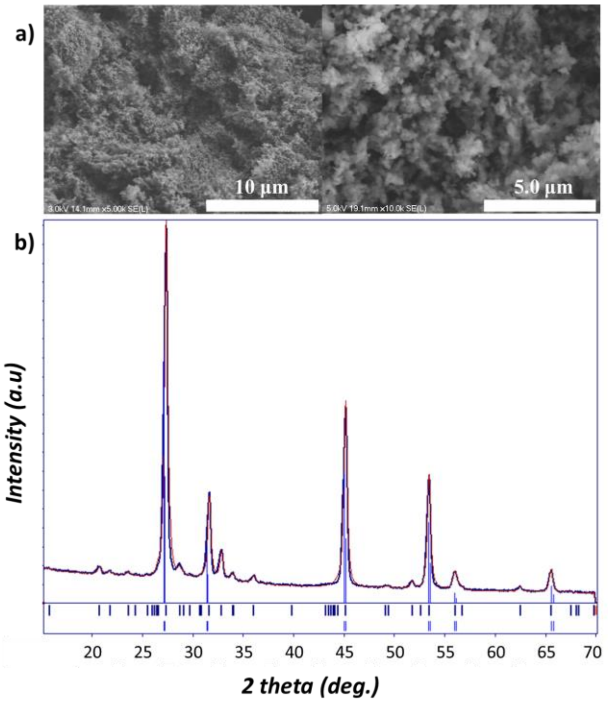

Figure 2. a) SEM image of plasma-synthesized Li_2S and b) its XRD pattern.

Figure 3 depicts the typical cyclic voltammetry of Li_2S. The first cycle shows a single charge (or anodic) peak at 3.6 V related to the kinetic barrier that has to be overcome in order to achieve the lithium extraction. At this potential, Li_2S is oxidized to lithium polysulfides and sulfur (for most C-coated Li_2S, this oxidation takes place around 2.4 V). Two discharge peaks are observed at 2.02 V and 2.34 V and represent the electrochemical reduction of lithium polysulfides to short-chain polysulfides and to Li_2S. Subsequent cycles show a sharp peak below 2.5 V that indicate the fast Li^+ diffusion at the given potential, mostly attributed to the small particle size. Furthermore, as the number of cycles increases, the area of the peaks decreases and so does the capacity of the material, which is most likely related to the formation of byproducts due to the absence of a stable SEI layer. When compared to the cyclic voltammetry of carbon-coated samples reported in the literature, it is clear that, by protecting the surface of the nanoparticles with carbon, larger cycleability would be obtained most likely due to the suppression of parasitic reactions [15]. Moreover, the electrolyte used for this preliminary test does not contain additives (*e.g.* $LiNO_3$ or P_2S_5) that have been reported to help stabilizing the SEI layer and to passivate the Li electrode [16].

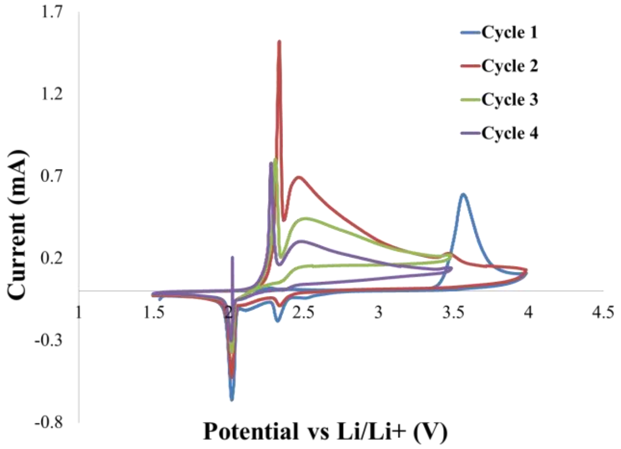

Figure 3. Cyclic voltammetry of Li_2S electrode against Li/Li^+ at scan rate of 0.1 mVs^{-1}.

3. Conclusions

Although the synthesis of Li_2S was successfully achieved by means of inductively coupled thermal plasma, the electrochemical stability of the positive electrode material is yet to be improved. In this sense, next steps include the use of electrolyte additives such as P_2S_5 and $LiNO_3$ that would help preventing the formation of parasitic reactions with the electrolyte while cycling. Furthermore, addition of a carbon coating that would increase the electronic conductivity and, at the same time, passivate the surface reactivity of the Li_2S nanoparticles, is expected to improve its stability and electrochemical performance.

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