Upscalling mesoporous graphene production through atmospheric pressure plasma technology for enhanced Li-based batteries.

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Since it was discovered in 2004, graphene has been hailed as *"the material of the future"* due to its remarkable properties and fascinating applications, including energy storage and innovative battery design [1,2]. Different methods have emerged for graphene synthesis, being the Hummers method the most fundamental approach. This method produces a low-quality product through a harmful process to the environment. More recent methods have enabled the production of high-quality graphene from highly oriented pyrolytic graphite (HOPG) by techniques such as mechanical exfoliation or laser ablation. However, these techniques lack of scalability, limiting their potential for meeting industrial requirements. Nevertheless, several methods have been developed to generate high-quality graphene that allows scalability, although they show different drawbacks. Among them, liquid phase exfoliation (LPE) and chemical vapor deposition (CVD) stand out. Therefore, none of this methods offers a single-step, low-cost approach for obtaining high-quality graphene powder.

Plasma technology represents a significant advance in this field. Microwave plasma torches (Fig. 1) exhibit high reactivity, making them capable of inducing decomposition reactions with a high efficiency (~100%), surpassing traditional chemical processes. Organic molecules are broken into atomic components, leading to the formation of compounds different from the original ones when the atoms recombine at the plasma outlet. At atmospheric pressure, the numerous collisions between electrons and heavy particles favor the nucleation process of materials, such as graphene as it has been reported using ethanol as a carbon precursor [3]. It is an eco-friendly, cost-effective and scalable method for high-quality graphene generation in a single-step process. So, it is deeply engaging to optimize the technique. To enhance the quantity of synthesized graphene, a process refinement has been conducted based on two key parameters: the amount of ethanol considered [4] and the applied power [5]. It was discovered that microwave power proves to be the optimal parameter for upscaling the process, resulting in an increase in graphene production rate from 79.3 mg/h to 111.3 mg/h when the power was raised from 350 W to 500 W [5]. This increase also enhances energy yield, as a 40% increase in graphene production rate was achieved with just a 30% increase in power. Moreover, it is achieved without compromising material properties: physicochemical characteristics of graphene powder have been analyzed using different analysis techniques: Raman spectroscopy, X-ray photoelectron spectroscopy, electron microscopy, thermogravimetry, and X-ray crystallography. No significant modifications were detected due to changes in applied power. Additionally, nitrogen adsorption/desorption tests as well as pore size distribution measurements of graphene obtained with both 350 and 500 W were carried out (Fig. 2). In both cases, isotherm curves show a type IV behavior, related to mesoporous materials, and a similar pore size

Fig. 1: Microwave plasma torch during graphene synthesis process.

distribution. Their porosity fits a bi-modal distribution, with a first zone of small mesoporosity (3-18 nm), and a second zone with large mesopores and some macropores (30-70 nm). The absence of microporosity is confirmed by t-plot method.

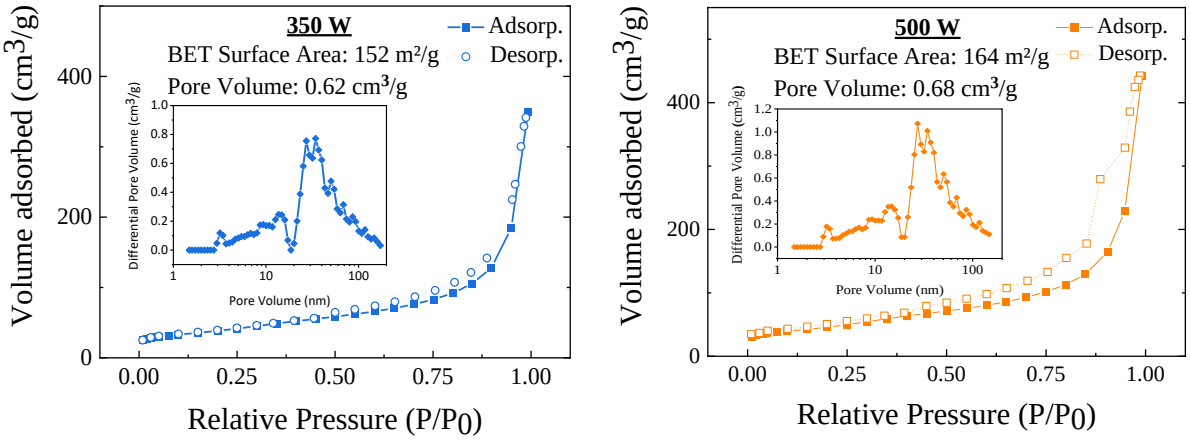

Fig. 2: Nitrogen adsorption/desorption curves and pore size distributions.

Once upscalled graphene yield, graphene synthesized through microwave plasma technology is found to be of particular interest for applications in the energy storage field, specifically in the design of high-performance Lithium-Sulfur (Li-S) batteries. During discharge, the lithium metal anode undergoes oxidation, releasing lithium ions and electrons that migrate to the sulfur cathode. However, during the electrochemical reactions at the positive electrode, the cyclic sulfur molecule (S_8) is reduced, leading to the formation of a series of polysulfides (Li_2S_n), some of them in solution. Here lies one of the main drawbacks of these batteries: the shuttle effect [6], which involves the migration of polysulfides during charge and discharge cycles. This causes the formation of polysulfide deposits on the lithium electrode, which results in a loss of battery capacity and faster degradation of performance over time, diminishing energy efficiency and reducing lifespan. However, the porosity properties of graphene can fight the shuttle effect, capturing polysulfides in solution as shown in Fig. 3. The first picture depicts the dissolution of Li_2S_6 polysulfide in a dioxolane (DOL) and dimethoxyethane (DME) mixture (DOL:DME, 1:1) to mimic the electrolyte environment used in batteries. The yellow color characteristic of high-order polysulfides is clearly visible. In the subsequent image, graphene powder is incorporated. After two hours, it is observed that the solution has become colorless, indicating the adsorption of these polysulfides by the graphene matrix. So, to improve Li-S batteries performance, we propose the integration of a sulfur-graphene composite that acts as a highly-efficient positive electrode.

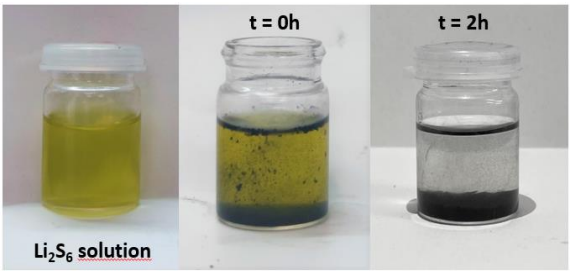

Fig. 3: Polysulfides capturing by graphene

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