Microwave-Induced Temperature Fields in Graphite Powder Heated in a Waveguide Reactor

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Abstract — Microwave-enabled exfoliation of graphite oxides has been recently shown to be capable of quickly producing graphene sheets of larger size and with fewer defects with the potential for low-cost mass production. In this paper, we investigate microwave heating of graphite powder in a waveguide reactor using multiphysics macroscopic modeling and experimentation. High heating rate and strong non-uniformity of temperature field are demonstrated and discussed as the key characteristics that require rigorous control in processes involving microwave heating of graphite powder.

Index Terms — Graphene, graphite, loss factor, microwave heating, thermal conductivity, temperature, waveguide reactor.

I. Introduction

The extraordinary (electrical, magnetic, thermal, mechanical, etc.) properties of graphene are expected to lead to revolutionnary technologies in many areas, such as solar cells, lithium-ion batteries, and medical diagnostics, to name a few [1].

Chemistry currently plays an increasingly important role in the development of practical techniques of graphene production [2]-[3]. There are a number of chemical methods for generating graphene from graphite, but only a very few techniques, such as exfoliation of graphite oxide (GO) [2]-[3], appear to be scalable and afford the possibility of high-volume production. Since the exfoliation process must be carried out at high temperatures, there are reports (e.g., [4]-[5]) about using microwaves as an alternative energy source in producing graphene from GO. These studies were conducted in the systems providing poor means of control over the microwave characteristics, and the processes have never been analyzed in terms of interaction of the microwaves with the reactants. Yet, knowledge of electromagnetic (EM) and temperature fields may be helpful in explaining particular effects, in developing the process controlling the quality of graphene, and in designing enlarged microwave systems for up-scaled production.

In this paper, we are concerned with the method of microwave-enabled production of graphene from graphite powder in a mixture of nitric and sulfuric acids [5]. On the level of lab tests, this method demonstrates a very short production period, a capacity for producing graphene sheets of much larger size and with fewer defects, and the potential for low-cost mass production. Here we consider the rtelated process of microwave heating of graphite powder in terms of heating rates, temperature fields, and the means of control of this process.

II. Problem

The issue of controllability is very difficult to address in its entirety, so here we are limited to a macroscopic consideration of microwave heating of graphite powder alone. Indeed, due to its unusual EM and thermal properties, graphite is infamous for its abnormal and hardly predictable responses to microwave irradiation. The scenarios involving microwaved graphite powder were considered earlier (e.g., [6]-[7]), but the analyses have been focused on structural parameters rather than the EM and temperature characteristics. So, microwave heating of graphite powder is still poorly understood and should be considered prior to the study of graphite mixed with the acids. Since the prime physical phenomena in graphene production [5] are enabled by interaction of the reactant with the EM field, some valuable observations about this process can be made on a macroscopic level. Some related studies have been recently attempted in [8] and proved to be informative.

This paper outlines our experimental and modeling results for graphite powder in a waveguide reactor fed by a solid-state generator. We describe an FDTD-based multiphysics model including the material parameters of the graphite powder. We show the presence of strong hot spots in the thin surface layer; very high heating rates are also detected. Measurements of internal temperature of the reactants show an acceptable consistency of the experimental and modeling results.

III. Experimental System

The system shown in Fig. 1 is designed, manufactured, and put on the market (under the name of *MiniFlow 200SS*) by SAIREM SAS, Nyron, France. The reactor is built on a bended WR430 waveguide section with an enlarged cylindrical space for the reactant. This space is bounded by a cylindrical Teflon tube (internal diameter 60 mm, height 94 mm) and accessible (for measurements and visual observation) through two (vertical and horizontal) metal tubes serving as cutoff waveguides not allowing for leakage from the reactor. The system is fed by a solid-state generator providing a robust control over the frequency (from 2.43 to 2.47 GHz with the step of 0.1 MHz) and the level of microwave power (from 0 to 200 W with the step of 1 W). On the opposite end, the terminal section of the system contains a sliding shoring wall aiming to control the wave propagation in the reactor.

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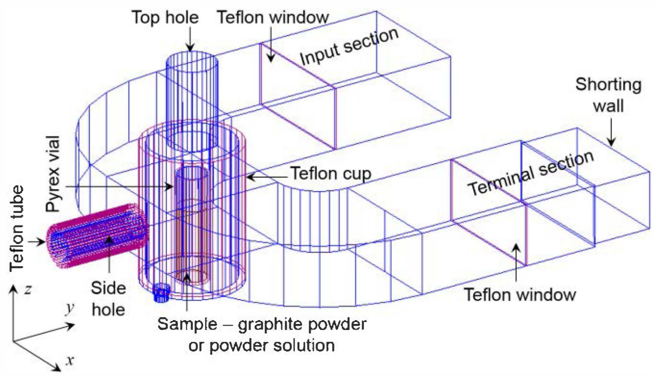

Fig. 1. 3D view of the internal structure of SAIREM's *MiniFlow 200SS* waveguide reactor.

TABLE I
COMPLEX PERMITTIVITY OF GRAPHITE POWDER AT 2.45 GHZ

Ref.	[12]		[8]
Particle sizes (μm)	80		< 20
Density (g/cm^3)	0.215	0.256	0.276
ε'	25.8	18.8	21.6
ε''	11.2	14.2	27.5

TABLE II
THERMAL PARAMETERS OF GRAPHITE POWDER

Temp. (°C)	C_p (J/(cmC))	ρ (g/cm^3)	k (W/(cmC))
20	0.693	0.276	0.0087
40	0.75[illegible]	0.276	0.0081
60	0.807	0.276	0.0076
80	0.864	0.276	0.0071
100	0.919	0.276	0.0067
120	0.972	0.276	0.0062
140	1.023	0.276	0.0058
160	1.072	0.276	0.0055
180	1.118	0.276	0.0051
200	1.162	0.276	0.0048

In the experiments, we worked with synthetic graphite powder of diameter of particles < 20 μm (Sigma-Aldrich Co., LLC). Internal temperature of the reactant was measured by a fiber optic sensor (Neoptix, Inc.) held, except its tip, inside a glass capillary (internal diameter 2 mm) and placed at different points along the axis of the cylindrical samples.

IV. COMPUTER MODEL

A. Computational Procedure

The *MiniFlow 200SS* waveguide reactor (Fig. 1) was reproduced in a fully parameterized model developed for the full-wave 3D conformal FDTD simulator *QuickWave-3D 2013 QW-3D*) [9]. Simulations of the EM and temperature fields have been carried out following an iterative computational scheme for EM-thermal coupled problems [10]. The procedure was implemented using the core EM solver of the *QW-3D* package and a dedicated procedure for solving the heat transfer problems – the *QW Basic Heating Module*.

Simulations were run on a Dell T-4700 workstation with 16 GB RAM and two quad-core Intel Xeon 3.20 GHz processors.

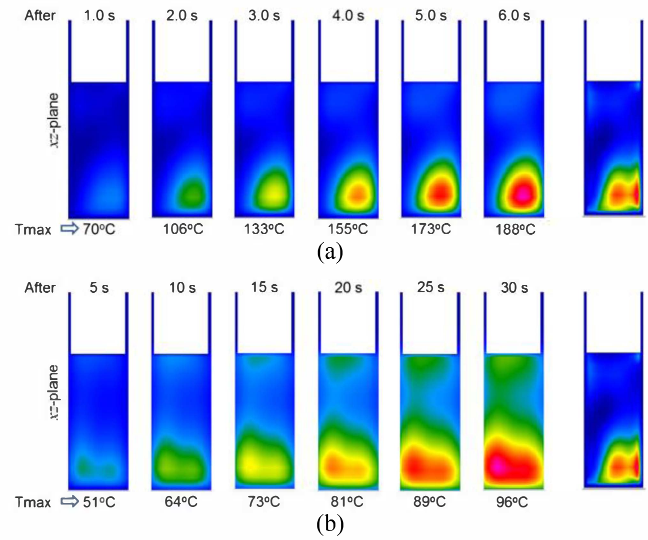

Fig. 2. Simulated evolution of temperature fields (initial temperature 23 C) in the coordinate plane through the cylindrical (diameter 20 mm, height 50 mm) sample of graphite powder in the Pyrex vial (outer diameter 23 mm, height 74 mm) in the *MiniFlow 200SS* waveguide system with the traveling (a) and standing (c) waves and with the dissipated power (far right patterns).

The scenario was discretized with a non-uniform mesh (with max cell sizes of 3.8 mm in air and 0.8 mm in the reactant) making 1.4 million cells. A single EM computation took about 3 min; in the coupled problem, simulation of temperature was completed in 40 s of CPU time.

B. Material Parameters of Graphite Powder

Complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ of graphite powder used in our experiments was measured at a room temperature with the use of an open-shield coaxial cell method [11] and reported in [8]. In Table 1, we compare the values of dielectric constant ε' and the loss factor ε'' with the data obtained in [12] by a similar technique; the results seem to be consistent. We use the values from [8] and assume ε' and ε'' to be temperature-independent.

Specific heat. In determination of thermal material parameters, we consider graphite powder as a mixture of graphite solid and air. For the specific heat C_p of solid graphite, the model of a temperature characteristic was suggested by Butland and Maddison [13] and later adopted as a standard reference. Table 2 contains a set of calculated values of C_p; we assume that specific heat of graphite powder is the same.

Density. For graphite powder in our experiments, the apparent (or bulk) density ρ is found to be ρ = 0.276 g/cm^3. Except very high temperatures of graphitization, the apparent density does not depend on temperature.

Thermal conductivity. Graphite's thermal conductivity is highly anisotropic: at room temperature, the values of in-plane thermal conductivity $k_{||}$ of highly oriented graphite can reach 20 W/(cmC), but in the perpendicular direction, $k_{\perp}$ is reported to be around 0.06 [14]. When powder is produced from graphite solid, the orientation of graphite platelets in the basal plane may be broken and the conditions for exceptionally high thermal

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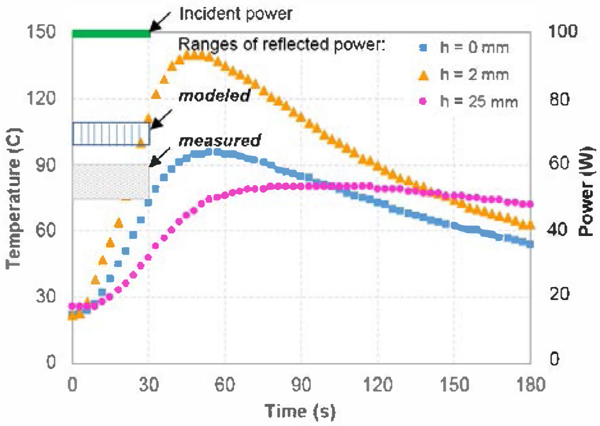

Fig. 3. Temperature evolution in different positions *h* along the axis of the cylindrical sample (diameter 20 mm, height 50 mm) of graphite powder in the Pyrex vial (outer diameter 23 mm, height 74 mm); incident microwave power is applied for 30 s; reflected power (measured and simulated) for a non-resonant regime (s = 104 mm).

conductivity become available for all directions. We thus conclude that in the mixture models for thermal conductivity of graphite powders, the solids fraction consisting of small graphite particles may be characterized by $k_{\|}$. This, on the other hand, implies that the thermal conductivity ratio for the graphite powder's fractions is very high ($k_{\|}/k_{air} > 10^4$).

The approach suggested by Hsu *et al* [15] for calculating thermal conductivity of porous media modifies the Zehner-Schlinder model for a packed-sphere bed with finite contact areas (rather than point contacts) between spheres – such finite-area contacts may support higher conductivity of the embedded substance. It has been shown that this modified Zehner-Schlinder model is in a good agreement with experimental data at the values of thermal conductivity ratio up to about 10^4 [15]. Therefore, it appears to be applicable for finding the effective thermal conductivity k of the graphite/air mixture.

In accordance with this model, k depends on the porosity of the mixture which, in its, turn, depends on the density of the related solid. The true density of solid graphite ρ_s is known to be 2.1-2.3 g/cm^3. As graphite is a porous material, in reality its density is less: e.g., Poco Graphite, Inc. produces poly-crystalline graphite in the density range $1.3 \leq \rho_s \leq 1.9$ g/cm^3.

Numerical values of k calculated with the modified Zehner-Schlinder model [15] for ρ_s = 1.6 g/cm^3, the data on temperature-dependent $k_{\|}$ of graphite solid [14] and the value k_{air} = 2.57×10^{-4} (W/(cmC)) [16], are presented in Table 2.

V. Results

The studied scenario involves the cylindrical sample of graphite powder in a Pyrex vial centrally put in the reactor and processed by 100 W of microwave power at 2.45 GHz.

Our computations show that EM and thermal characteristics of microwave heating of graphite powder in the *MiniFlow 200SS* waveguide system strongly depend on the position of the sliding shorting wall. With the distance s from the wall to the Teflon window near 89 mm, the system is tuned on a resonance mode, a traveling wave is observed in the section preceding the sample, and most part of the microwave energy is absorbed by the graphite sample. Being an exceptionally lossy material, it is heated extremely quickly: the max temperature reaches ~200ºC in 6 s (Fig. 2(a)). Out of the resonant mode, the sample absorbs less microwave power, the heating rates significantly drops, and the temperature pattern appears to be very different (Fig. 2(b)).

Both modeling and measurement show extremely non-uniform heating with hot spots near the surface. With micro-wave power turned on, the sample is heated only by micro-waves: heat diffusion makes no effect in the temperature patterns, which are nearly identical with the related patterns of dissipated power (Fig. 2).

The time-temperature characteristics measured on the axis of the sample at different distances h from the bottom are shown in Fig. 3. Temperatures at those points (located beside the hot spots) continue to grow after shutting microwaves down – for 30-60 s after 30 s of applying microwave power. The influence of the shorting wall on the heating rate is also shown.

The levels of reflected power were also both measured and simulated; the resulting ranges are shown in Fig. 3. Given the intrinsic uncertainty in depiction of material parameters of graphite powder, the presented degree of closeness of the experimental and modeling results can be viewed satisfactory.

VI. Conclusion

The constructed computer model for the process of microwave heating of graphite powder in a waveguide reactor has been reported. The model is based on the set of (experimentally determined and theoretically derived) EM and thermal material parameters of graphite powder. In the model these parameters are specified with intrinsic uncertainty, but our simulations show the system behavior is consistent with the experimentally observed. It has been shown that, due to its high loss factor and low thermal conductivity, graphite powder is heated very quickly and very non-uniformly. These features are expected to make an impact on the characteristics of different microwave heating scenarios with graphite powder and should be addressed in future works; the developed modeling approach may be a practical and instructive instrument in those studies.

Acknowledgments

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