Arc discharge in methane with a molten metal anode for synthesis of SWCNTs

S. Musikhin[1], Y. Raitses[1], V. Nemchinsky[1], H. Gu[2], B. E. Koel[2]
[1]*Princeton Plasma Physics Laboratory, Princeton, USA*
[2]*Chemical and Biological Engineering, Princeton University, Princeton, USA*

Abstract: This study investigates a novel DC arc with a molten metal anode in methane for SWCNT synthesis. Comprehensive analysis reveals methane decomposition in the arc and co-production of metal catalyst and SWCNTs. The effects of metal particle encapsulation with carbon and metal anode carburization are discovered and explained, offering ways to optimize the process through controlled catalyst production rate and catalyst particle size.

1. Introduction

DC arc discharge remains a primary method for large-scale production of single-walled carbon nanotubes (SWCNTs). Commonly, the discharge is maintained between graphite electrodes with a metal catalyst added as a powder of microparticles. An alternative approach is to use hydrocarbon gas as a carbon feedstock, e.g., natural gas or methane.

The use of methane (CH_4), a greenhouse gas, as a source, makes the approach sustainable and scalable, although its optimization is still ongoing [1]. Here, we focus on two optimization parameters: (i) the size of metal catalyst particles, which was shown to affect the selectivity of CNT synthesis and their thickness [2]; and (ii) the carbon/catalyst ratio, which should be adjusted to maximize CNT yield without wasting excessive amounts of precursor or catalyst.

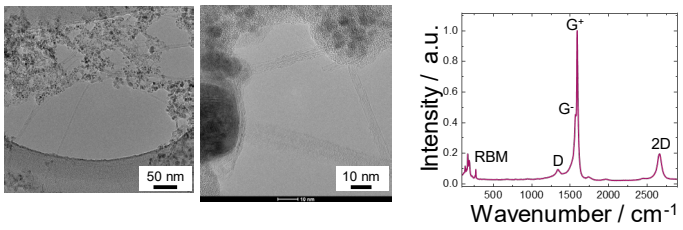

Fig. 1. Transmission electron microscopy images and a Raman spectrum of the produced non-purified nanomaterials.

2. Methods

Experiments were conducted in a vacuum chamber with the DC arc maintained between a cathode made from 2% ceriated tungsten and an anode made from either low-carbon steel (ASTM A36) or pure iron. Gas mixtures of Ar and CH_4 in different proportions were investigated. In all cases, the total pressure was 500 Torr (67 kPa). The arc was operated at currents between 30—50 A and voltages between 10—20 V. The arc and electrodes were characterized in situ using high-speed imaging, optical emission spectroscopy, and thermal imaging. The synthesized nanomaterials were extensively characterized ex situ.

3. Results and Discussion

Spectrally resolved imaging of the arc at 515 nm (C_2) and 656 nm (H_α) confirmed that CH_4 was pyrolytically decomposed inside the hot arc core. The catalyst production rate was estimated by measuring the anode ablation rate. However, it was found that both steel and iron anodes were carburized during the experiment, and hence, their ablation rate could not be measured by weighing the anode before and after the run. Instead, the anode temperature was measured by thermal imaging, which was used to estimate the anode ablation rate. Carburization was shown to significantly reduce the anode temperature.

Figure 1 shows transmission electron microscopy images and a Raman spectrum of the obtained nanomaterials. The spherical iron nanoparticles were either surrounded by carbonaceous shells or connected to bundles of SWCNTs. The Raman spectrum additionally confirmed the presence of SWCNTs in the sample. By comparing the size of iron nanoparticles produced with and without the addition of CH_4 in argon, we built a theoretical model explaining the limiting effect of a carbon shell on iron particle size [3]. While the carbon shell is gradually forming on the iron particle surface, it inhibits particle growth until it is fully encapsulated, at which point the metal particle growth ceases. We claim that this effect alone is sufficient to limit metal nanoparticle growth to a size of just a couple of nanometers and that, if controlled, this effect could be beneficial to SWCNT formation.

4. Conclusion

A suite of diagnostics applied to a novel DC arc with a molten metal anode in methane confirmed that: (i) Methane is decomposed inside the arc core; (ii) Catalyst nanoparticles and SWCNT are co-produced; (iii) Carbon encapsulation inhibits metal catalyst growth; and (iv) The metal anode is carburized, which affects its temperature and ablation rate. The results demonstrate a path to optimize the process efficiency, e.g., to control the catalyst production rate and to manipulate metal particle size in a methane arc environment.

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References

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