

# Magnesiothermic Reduction of Carbon Dioxide in a Porous Monolith for Carbon Dioxide-Derived Carbon Materials

Hadas Elazar-Mittelman<sup>1,2,3</sup>, Peter Corkery<sup>2</sup>, Michael Tsapatsis<sup>2,4\*</sup>, Jonah Erlebacher<sup>1,3\*</sup>

*1 Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, USA; 2 Department Chemical and Biomolecular Engineering & Institute for NanoBioTechnology, Johns Hopkins University, Baltimore, Maryland 21218, USA; 3 Ralph O'Conner Sustainable Energy Institute, Johns Hopkins University, Baltimore, Maryland 21218, USA; 4 The Johns Hopkins University Applied Physics Laboratory, Laurel, Maryland 20723, USA.*

*\*Corresponding authors: , tsapatsis@jhu.edu*

## Highlights

- Magnesiothermic reduction presents the opportunity to transform CO<sub>2</sub> to solid carbon.
- Various reaction schemes explored to tailor deposition profile within a monolith.
- Bulk C-MgO materials produced have potential to be used as a carbon-negative structural material.
- C-MgO materials produced have a range of applications in sustainable technology.

## 1. Introduction

Carbon capture, sequestration and utilization (CCSU) will undoubtedly be a key component of a sustainable carbon future. Current permanent carbon dioxide (CO<sub>2</sub>) sequestration methods focus on geological storage, however, great opportunities exist in engineering CO<sub>2</sub>-derived high-value and high-volume manufacturing carbon materials, such as graphitic carbon and carbon composites, with negative lifecycle emissions called “negative-carbon carbon” (NCC) materials. Previous studies have prepared carbon materials using metallothermic reduction reactions (MRRs) of CO<sub>2</sub>, in which metal vapors react with CO<sub>2</sub> to form metal oxides and elemental carbon [1]. The MRR between Mg and CO<sub>2</sub> has stood out as a particularly useful MRR, referred to as magnesiothermic reduction (MR) of CO<sub>2</sub>, as it yields a range of carbon and magnesium oxide (C-MgO) based products with resulting morphologies dependent upon reaction temperature, concentration of CO<sub>2</sub> in the feed, and Mg precursor type [2]. This reaction system was first of interest for its application as a fuel for space travel in CO<sub>2</sub> rich environments, and early literature focused on fundamental reaction kinetics and thermodynamics of Mg particles burning in a CO<sub>2</sub> environment [3]. Other studies focused on heating Mg precursors, such as powders and ribbons, in batch reactors to yield particulate nanostructured carbon for applications in supercapacitors and as electrode materials [1]. Here, we aim to fabricate bulk materials, such as a structural carbon composite, and we study various reaction schemes within a porous monolithic carbon foam to provide a substrate for C-MgO product deposition. Unlike batch reactors that operate under well-mixed conditions, the reaction environment in the monolith varies with position and time based on the coupling of reaction and heat and mass transfer-phenomena. To achieve uniform deposition within the pores, one has to control the evolution of the concentration profiles over the duration of the reaction. This study demonstrates the construction of a custom reactor and the synthesis and characterization of the of materials described above towards further development of the MR of CO<sub>2</sub> as an approach of CCSU to produce bulk C-MgO composite materials.

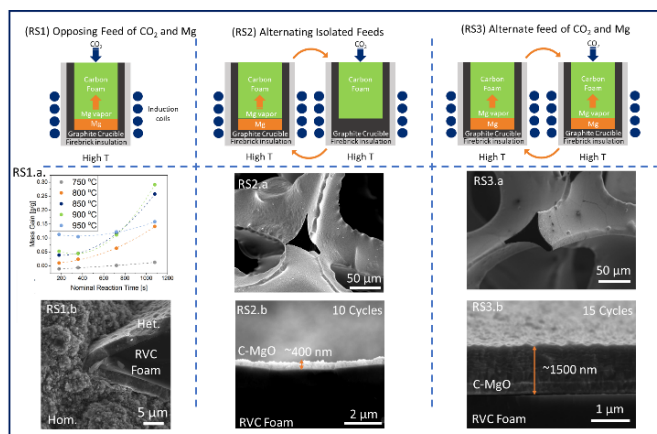
## 2. Methods

A custom reactor was constructed to allow for opposing flows of Mg vapor and CO<sub>2</sub> gas, rapid heating via a radio-frequency induction furnace (4.2 kW Ambrell Easyheat Induction System), and control via a LabView virtual instrument. The reactor was loaded with an insulated crucible containing 0.3 g of reticulated vitreous carbon (RVC) foam (100 pores per inch (PPI)) (ERG) and a 3g Mg disc (Trolleyshop). Programmed reactions were controlled by the LabView VI which specified process temperature, pressure, and the valving sequence for introducing CO<sub>2</sub> and Ar into the reactor. Three reaction schemes were investigated: Reaction scheme 1 (RS1) involved concurrent opposing flows of Mg vapor and CO<sub>2</sub> gas, reaction scheme 2 (RS2) alternated between Mg vapor and CO<sub>2</sub> gas, and reaction scheme 3 (RS3) switched the CO<sub>2</sub> feed on and off while maintaining the Mg vapor feed. The prepared materials were characterized using a Rigaku Miniflex X-ray Diffractometer (XRD) with a CuK $\alpha$  source, a Horiba LabRam Evolution Raman Spectrometer (532 nm laser line and 100  $\mu$ m spot

size), and a Tescan Mira 3 GM Scanning Electron Microscope (SEM) (5kV excitation voltage) equipped with EDAX Octane Elite Energy Dispersive X-ray Spectroscopy (EDS) system. Deposit thickness was measured from SEM micrographs using ImageJ.

### 3. Results and Discussion

To investigate the effect of the reactant feed conditions and sequence, three reaction schemes designed and are shown as RS1, RS2, and RS3 in **Figure 1**. The three reaction schemes studied each yielded a different deposition profile over the monolith and overall product yield while maintaining the same C-MgO reaction product. The resulting product consisted of MgO nanoparticles encapsulated by a carbon matrix. The formation of MgO was confirmed by XRD and EDS, and Raman was utilized to characterize the structure of the formed carbon. RS1, which employs simultaneous opposing flows of Mg vapor and CO<sub>2</sub>, demonstrates an increase in mass deposited as reaction time and temperature increase, with the highest product yield observed at 900 °C and 1080 s (**Figure 1, RS1.a**). RS1 yields two product morphologies: a homogenous product likely formed via a gas-phase reaction between CO<sub>2</sub> and Mg vapor, and a heterogenous product that deposited on the surface of the monolith support (**Figure 1, RS1.b**). RS1 consistently resulted in an uneven deposition profile of the reaction product over the monolith, where the location of the steady-state reaction front and distribution of the deposition is a function of the temperature and concentration of CO<sub>2</sub> in the feed. RS2 was utilized with the goal of selectively forming a film of the heterogenous product on the surface of the support (**Figure 1, RS2.a**). This was achieved by cycling the following steps: depositing a layer of Mg via thermal evaporation in the presence of Ar, removing the Mg source, then uniformly exposing the now Mg coated monolith to CO<sub>2</sub> and heating. Here, the extent of reaction is limited by the Mg previously deposited, and the layer thickness can be directly controlled as a discrete function of Mg deposition and CO<sub>2</sub> reaction cycles, depositing ~40 nm per cycle (**Figure 1, RS2.b**). To produce thicker films, RS3 was investigated as an approach to maximize deposition within the pores while maintaining selectivity of the heterogenous reaction ((**Figure 1, RS3.a and b**). Here, the timing and sequence of the cycles is determined by the transport properties of each reagent through the porous monolith. The reaction front and the amplitude of the fronts oscillations along the length of the monolith can be tuned as a function of the timing of the CO<sub>2</sub> feed, feed composition, and flow rate.



**Figure 1.** Results for the various reaction schemes studied for the RM of CO<sub>2</sub>.

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### 4. Conclusions

The MR of CO<sub>2</sub> was carried out within a porous carbon monolith via three reaction schemes to yield a suite of C-MgO composites. The cyclic reaction scheme allowed for the deposition of a uniform conformal layer of the C-MgO product on the porous monolith, and a transient reaction scheme was advantageous towards maximizing deposition while maintaining product morphology selectivity.

### References

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### Keywords

carbon; reaction-diffusion; carbon-utilization; metallothermic reduction