Fluidized Bed Production of Surface Functionalized Powders for Solid Oxide Fuel Cell (SOFC) Cathodes

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INTRODUCTION:

Fuel cells offer tremendous potential for highly efficient conversion of fossil fuels to electrical power. Solid oxide fuel cells (SOFC) are particularly attractive, since they can utilize hydrocarbon fuels. A main development goal for SOFC's is to reduce operating temperatures to the 600 C to 800 C range. The lower operating temperature will reduce manufacturing and operating costs, simplify design, and improve reliability and durability.

Presently, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) is the state of the art material for intermediate temperature SOFC cathodes [1-3]. LSCF maintains excellent electrical conductivity at lower temperatures, but suffers from reduced catalytic activity. LSCF also has long term stability issues [4]. An alternative cathode material is $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM). LSM shows excellent long term stability and high catalytic activity at low temperatures, but poor electrical conductivity. at low temperatures.

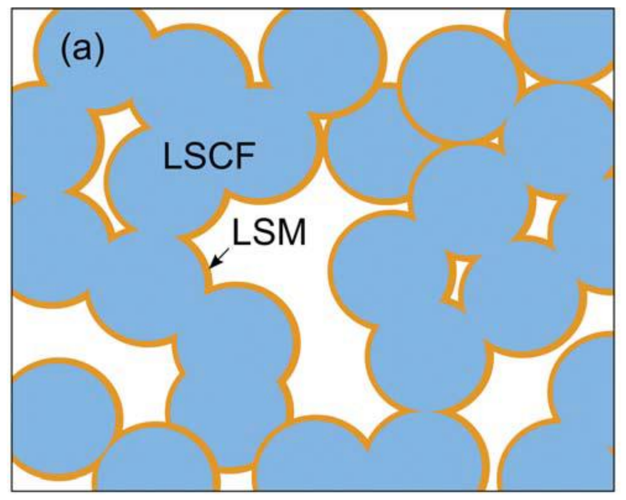

Figure 1: Ideal structure of LSM coated LSCF cathode. From Reference [5].

INTRODUCTION (Continued):

Recent work has shown that a thin LSM coating on an LSCF cathode improved both SOFC performance and stability [5]. The proposed electrode structure consists of an LSCF backbone and an LSM thin film coating, as shown in Figure 1. This "surface functionalized" cathode takes advantage of the high conductivity of the LSCF backbone and the excellent reduction catalyst properties of the LSM surface coating. Presently, the challenge is how to fabricate these surface functionalized cathode materials [6,7]. Thus far, development work has used liquid infiltration techniques to deposit the LSM surface layer on pre-fabricated porous LSCF cathodes. The liquid infiltration technique suffers from several drawbacks, including poor control of the LSM film thickness and poor coverage of the LSCF surface.

TECHNICAL APPROACH:

Structured Materials Industries, Inc. (SMI) is developing an alternative approach to produce surface functionalized cathode materials, based on fluidized bed chemical vapor deposition (FBCVD). FBCVD combines the two well established industrial techniques of fluidized bed processing of powders, and chemical

TECHNICAL APPROACH (Continued):

vapor deposition of oxide thin films [8]. The FBCVD process was developed by Structured Materials Industries (SBIR Award Number DE-FG02-07ER84765) to produce spherical powders with optically active surface layers [9]. Chemical vapor deposition (CVD) of oxide films is an established technology, which can be accomplished using metal organic precursors and oxygen [10]. However, conventional CVD processes do not work for coating powders, due to the need to keep the powder separated during deposition.

Fluidized bed processing is a well established technique, which is used in a variety of commercial applications [11]. Figure 2 shows a schematic diagram of a traditional fluidized bed reactor. Chemical vapor deposition in a conventional fluidized bed reactor is difficult, since the process gases can react

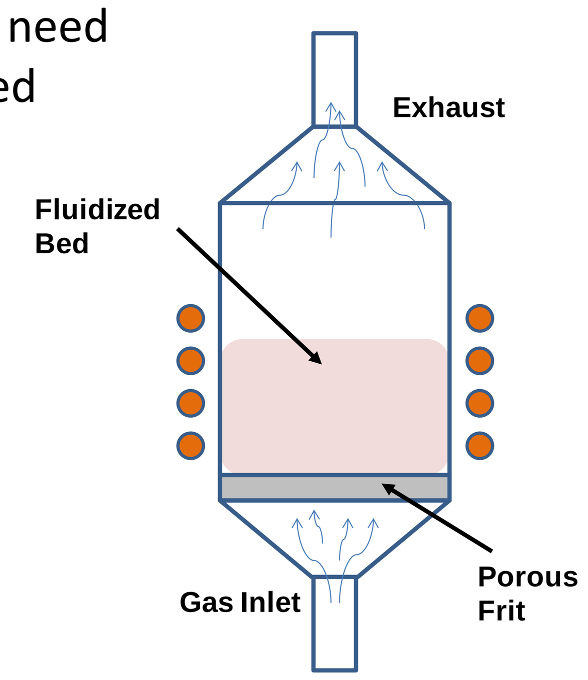

Figure 2: Schematic diagram of conventional fluidized bed reactor.

TECHNICAL APPROACH (Continued):

inside the porous frit and cause clogging. To prevent this issue, SMI developed the top down injector FBCVD design, as shown in Figure 3. The FBCVD reactor consists of a closed-end ceramic tube. External heating is applied using a standard tube furnace. One of the advantages of SMI's design is the ease of scaling to large volume production, simply by using larger tube and furnace sizes. Figures 4 through 6 show examples of materials processed using SMI's FBCVD technology.

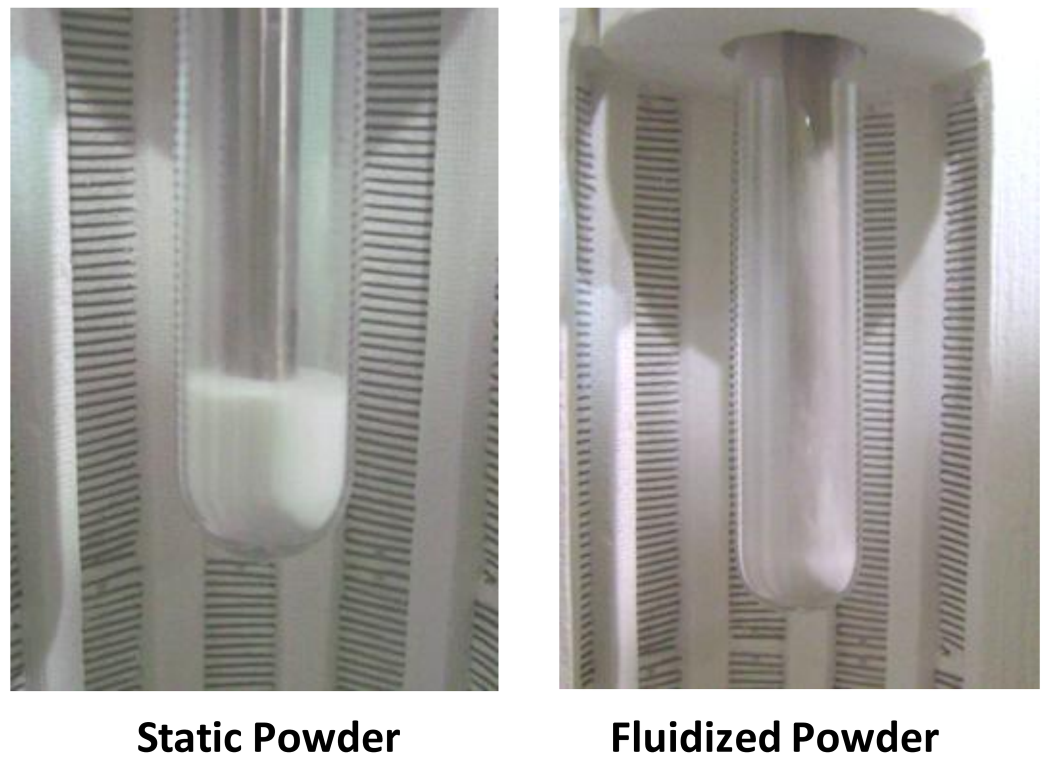

Figure 3: Top down injection fluidized bed CVD reactor at SMI mounted in a clam shell furnace.

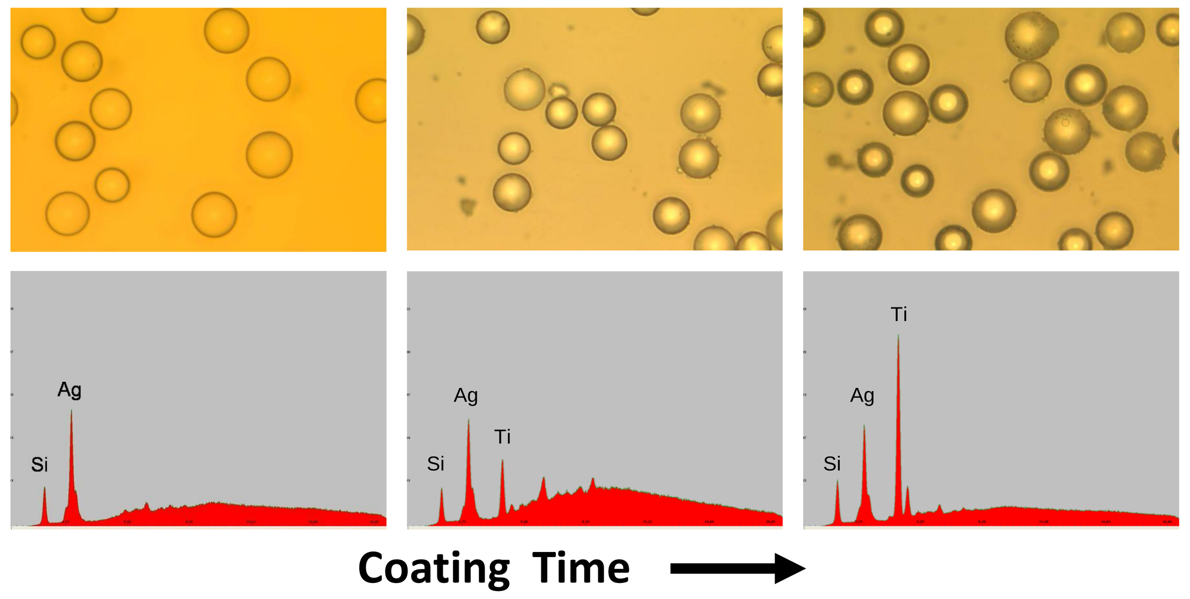

Figure 4: Spherical SiO_2 powder (50 µm diameter) with 1 µm thick $TiSiO_2$ coating deposited by FBCVD at SMI. (Upper) Optical microscopy images. (Lower) X-ray fluorescence spectra using Ag primary x-ray source.

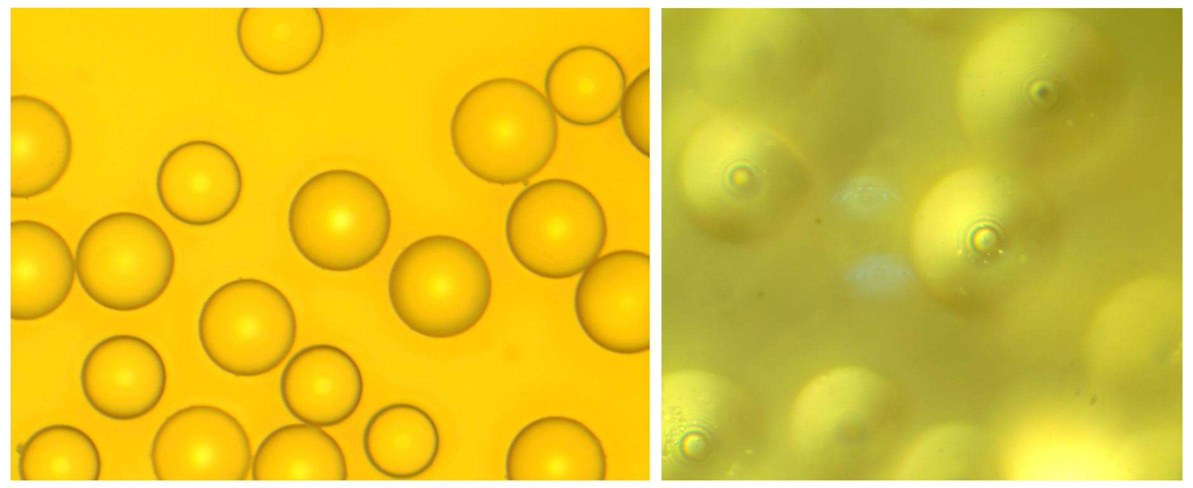

Figure 5: Spherical SiO_2 powder (50 µm diameter) with uniform GeO_2 coating deposited by FBCVD at SMI.

EXPERIMENTAL DETAILS:

LSM coatings are deposited from the metal organic precursors $La(thd)_3$, $Sr(thd)_2$ and $Mn(thd)_3$, in which "thd" = 2,2,6,6-tetramethyl-3,5-heptanedionato. Oxygen gas is used as the oxidizer and argon gas as the uniform flow. Figure 7 shows x-ray fluorescence results for an LSM film deposited on a silicon wafer. Once the CVD process for LSM is established and calibrated, the process will be transferred to the FBCVD reactor for production and demonstration of LSM coated LSCF powders.

Figure 6: Borosilicate glass beads (6 mm diameter) with $TiSiO_2$ coating deposited by FBCVD at SMI.

SUMMARY AND CONCLUSIONS:

The FBCVD process can produce a wide range of uniform coatings on powders, with excellent control of thickness and composition. The resulting surface functionalized LSCF powders can be

SUMMARY AND CONCLUSIONS (Continued):

processed into SOFC cathode materials using standard tape-cast and sintering techniques. The FBCVD technique is scalable to high volume production, and can provide surface functionalized LSCF powders at competitive costs, for future SOFC implementation.

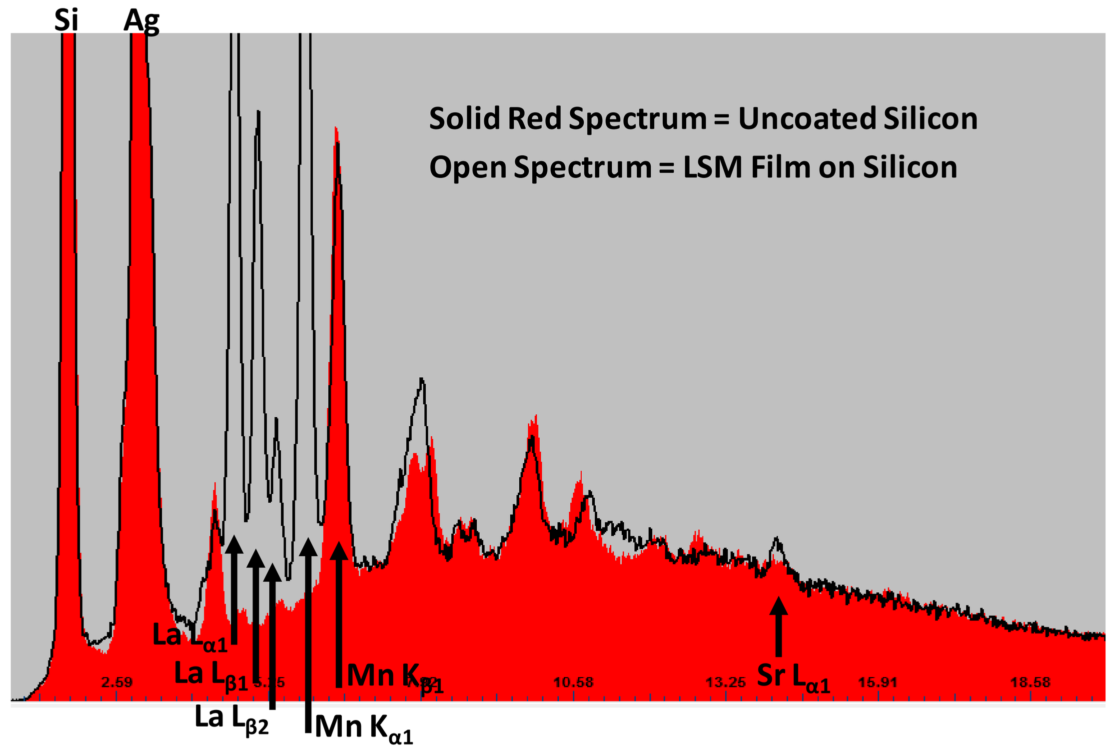

Figure 7: X-ray fluorescence spectrum of an LSM film deposited on silicon by CVD at SMI.

ACKNOWLEDGEMENTS:

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