INNOVATIVE, LASER-BASED PROCESS FOR DEVELOPMENT AND MANUFACTURING OF SOLID OXIDE FUEL CELLS

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ABSTRACT

A novel, versatile, scalable and economical laser-pyrolysis based process for high performance solid oxide fuel cells (SOFCs), interconnects and seals is described. The Laser Reactive Deposition (LRD™) process converts low cost metal precursors into SOFC layers; thus eliminating the need to undertake powder synthesis, calcining, ball milling, batch formulation, slurry preparation, tape formation, and binder burnout steps required in conventional SOFC cell fabrication. By simplifying the manufacturing process, the LRD™ route achieves low SOFC stack manufacturing cost at low volumes, simplifies footprint and throughput scale-up, and dramatically compresses materials and components development cycles, thus accelerating commercialization and market growth. Results from initial efforts to synthesize conventional SOFC layers (Ni-8YSZ anode, 8YSZ electrolyte, and Sr-doped LaMnO₃ cathode) by the LRD™ route from mixtures of the respective metal nitrates are described. The layers fabricated on 8YSZ substrates using the LRD™ approach are of the desired phase with crystallite sizes in the nanoscale region, even after sintering at high temperatures.

INTRODUCTION

Though the number of potential applications, and environmental and economic benefits, and therefore accessible markets, are large, solid oxide fuel cell (SOFC) commercialization is currently hampered by high fabrication costs and inadequate durability of stack components (1). Tape casting, screen printing, and/or tape calendaring are the current state-of-the-art in SOFC manufacturing. These methods require purchased ceramic powders as well as processing aides, typically organic, to transform the powders into green (or unfired) multilayers that are bisqued and densified into a SOFC cell. Tape-based processes are sensitive to the morphology (2) and composition (3) of the input powder. Powder synthesis is a complex operation that adds cost to the precursors. Additionally, using powder for process feedstock entails developing a supply chain and quality control of critical characteristics (purity, composition, phase, size, size distribution, surface area) while also limiting development options and increasing cycle times. Organic process modifiers used in these methods are undesirable as their purchase and incorporation into the process increases cost yet they do not add any value to the final product because they are pyrolyzed in the sintering step(s). The need to bisque (i.e. pyrolyze the organic binder system) for long periods at intermediate temperature and sinter the layers at high temperature make these the highest cost steps in conventional SOFC manufacturing (4). Furthermore, the sintering step creates the largest...
environmental impact due to the large energy requirements and volatile organic compounds generated during binder burnout (5,6).

The required large number of process steps and/or the raw material costs associated with developing improved materials and structures make present SOFC component fabrication methods relatively inflexible. Additionally, the difficulty in scaling up the individual unit processes create high development costs and long development cycle times. The number of individual process steps, process equipment, chemicals, and their suppliers involved in conventional SOFC processes cause forward cost projections to be dependent on a very large number of variables and therefore subject to a large degree of uncertainty. These complexities result in SOFC manufacturing cost targets predicated on plant production volumes in the several hundreds of MW; achieving present mass commercialization cost targets requires a 250 MW production volume in a single plant for conventional tape methods (4). Given that the forecast for SOFC stationary market in 2009 is approximately 200 MW (7), a significant fraction of the market will have to be captured for a plant to produce SOFCs at target cost. As a result a significant discrepancy exists between SOFC cost targets required for initial commercialization and subsequent market growth, and present SOFC manufacturing technology that can only meet those targets at high production volumes commensurate with mature market levels. This incongruity makes it clear that disruptive fabrication methods that provide versatility, scalability, and low-cost at both low and large volumes are needed to accelerate SOFC commercialization.

The Laser Reactive Deposition (LRD™) process is a recent invention initially developed to fabricate high quality thick glass films for planar lightwave circuits (8). Complex glasses such as Er-doped sodium aluminosilicates were deposited in thicknesses up to 40 \( \mu \text{m} \) on 150 mm wafers with optical signal attenuation levels of 0.1 to 0.05 dB/cm. Within-wafer uniformity and wafer-to-wafer repeatability of refractive index and thickness were at the levels of plasma-enhanced CVD (PECVD) at deposition rates though the deposition rates achieved with the LRD™ process were more than an order of magnitude higher than PECVD. LRD™ technology has recently been adapted to create a disruptive approach to SOFC fabrication (see Figure 1). LRD™ process comprises Laser Pyrolysis (LP) (9,10) for direct conversion of low-cost precursors, delivered to the reactor as an aerosol (section A in Figure 1) into submicron or nanoscale particles and uniform, high rate deposition (section B in Figure 1). During LP, one or more components of the precursor stream transfer the energy from the laser beam to the reactants, initiating nucleation events as the stream transverses and emerges from the Laser Reaction Zone (LRZ). The conditions in the LRZ are engineered to promote or inhibit growth, making particle size control straightforward. The newly

![Figure 1. Schematic of aerosol LRD™ process.](image-url)
formed particles are entrained in the spent process gas flow field and directed into contact with the deposition surface (section C in Figure 1).

The external ignition source provided by the laser beam results in a wide process window allowing materials to be synthesized in a range of environments. The unique capabilities provided by laser initiation of chemical reactions make the LRD™ process suitable for fabrication of porous and dense layers with virtually unlimited range of compositions, compositional complexity, and tailored microstructures at high deposition rates. Direct conversion of low-cost precursors (e.g. nitrates, chlorides) and high deposition rates combine to dramatically lower fabrication costs and development cycle times. Furthermore, the linearity of the laser ignition source makes LRD™ technology easily scalable to large cell footprints and high volume production.

Low-cost metal nitrate and chloride precursors, the same types used in many bulk SOFC powder processes, have been successfully utilized to synthesize all the materials used in SOFC anode (cermet of Ni/8 mol% Y₂O₃-stabilized ZrO₂ (11,12)), electrolyte (8 mol% Y₂O₃-stabilized ZrO₂ (13)), and cathodes (La₁₋ₓSrₓMnO₃ (14)) via aerosol spray techniques. The direct conversion of chemical precursors to SOFC layers along with the ability to control particle size and morphology provides LRD™ processes with unparalleled versatility. Past experience with LRD™ processing has demonstrated that critical layer properties are controllable through LRD™ process parameter settings. Among these properties are primary particle size, % porosity, thickness, compositional complexity and stoichiometry, phase, and number of layers. Accordingly, these characteristics can be varied by “dialing in” the experimental parameters. Therefore, LRD™ technology provides the ability to explore the three dimensions of electrode performance (composition, particle size, and porosity) in a single process step. New compositions can be evaluated by altering the ratio of metal precursors in the feedstock or adding new precursors. This facilitates the evaluation of synergistic effects among different dopants to increase performance and durability. Furthermore, particle size can be controlled down to the nanoscale regime with minimal cost impact. Nanoscale materials present an avenue for improving electrochemical performance as well as mechanical durability. The higher surface to volume ratio increases the triple-phase boundary region within porous electrodes thus lowering polarization. Additionally, the finer microstructure of nanocrystalline materials improves mechanical properties. The benefits of nanoscale materials have not been fully leveraged in SOFCs due to higher cost, limited availability of desired compositions, and incompatibility with conventional fabrication approaches. LRD™ technology eliminates these barriers providing a method to leverage nanoscale materials in optimizing fuel cell manufacturability and performance.

This paper reports results from initial efforts to synthesize conventional SOFC layers (Ni-8YSZ anodes, 8YSZ electrolyte, and Sr-doped LaMnO₃ cathode) by the LRD™ route from mixtures of the respective metal nitrates. Additionally, the prospects for using LRD™ technology for SOFC manufacturing are discussed.

**EXPERIMENTAL**

Samples were synthesized in a LRD™-200 reactor. This reactor is capable of depositing layers up to 200 mm footprint. The reactor pressure was set at 600 Torr; a throttle valve
was used to maintain pressure setpoint throughout the deposition. An industrial CO₂ laser (PRC Laser) was operated in continuous mode and focused using a ZnSe lens. Feedstock for the process consisted of aqueous solutions of ZrO(NO₃)₂, and Y(NO₃)₃ for electrolyte synthesis, Ni(NO₃)₂, ZrO(NO₃)₂, and Y(NO₃)₃ for the anode synthesis, La(NO₃)₃, Sr(NO₃)₂, and Mn(NO₃)₂ for the cathode synthesis. ZrO(NO₃)₂ and Mn(NO₃)₂ precursors were solutions whereas the others were powders. Deionized water was used as the solvent. A liquid MFC (Quantum) was used to meter liquid flow to the two-fluid atomizer. A combination of C₂H₄, O₂, and N₂ were used as process gases. The process gases were premixed and delivered through the atomizer to convert the liquid stream into an aerosol. For these experiments, material was deposited on the surface of 8YSZ discs (Intertec SW, Tucson, AZ) measuring 25 mm diameter and 200 μm thick.

XRD analysis was performed on a Rigaku Miniflex diffractometer using Cr Ka radiation and a V Kβ filter. Powder samples were dispersed on Si(511) zero background holders. Low background sample holders combined with the instrument’s variable slits, small goniometer radius and rotating stage result in acceptable signal/noise ratio at high diffraction angles. JADE 7+ (MDI, Livermore, CA) was used to analyze the XRD patterns. A Si powder reference was used to calibrate 2 Theta. A Micromeritics TriStar 3000 gas absorption analyzer was used to measure BET surface area. Microstructure analysis was performed using a Hitachi 3000H SEM.

RESULTS AND DISCUSSION

Figure 2 shows XRD patterns for 8YSZ powder synthesized in the LRD™-200 reactor and commercial 8YSZ powder (Tosoh TZ-8Y). Both patterns are similar. Table 1 shows the results of lattice parameter, size, and strain analysis for both materials. The size of the LRD™ 8YSZ is approximately 25% lower than TZ-8Y whereas the strain is significantly lower. Additionally, the lattice parameter of the LRD™ 8YSZ is lower than TZ-8Y. The BET surface area of the LRD™ 8YSZ was found to be 29.3 ± 0.2 m²/g. The equivalent spherical particle diameter calculated from the BET results is slightly higher than the X-ray crystallite size of 30 nm indicating that, macroscopically, the powder has a dense spherical morphology. Small particle size has been shown to lower zirconia sintering temperature to 1250°C or below if the particles do not contain hard agglomerates (13,15,16), even with green densities of 40% (16). The ability to densify 8YSZ layers at 1200°C enables co-sintering of LSM cathodes because this temperature is the threshold for formation of the insulating phase La₂Zr₂O₇ (17). These results show that the LRD™ route is a promising method to creating high quality 8YSZ electrolytes.

Figure 3 shows how phase content in Ni-8YSZ anode layers deposited in the LRD™-200 reactor were changed by modifying the ratio of the respective metal nitrates in the liquid feedstock. The increasing
intensity of the Ni and NiO peaks at the expense of the 8YSZ peak intensity shows that increasing the Ni/(Zr + Y) ratio in the feedstock, accomplished by adjusting the weights of the nitrate precursors, increased the amount of Ni(O) in the deposited layer. The relatively constant peak breadth and position indicate that crystallite size in the different layers is similar though the phase contents have changed. This result shows the relative simplicity of developing and optimizing new compositions using the LRD™ approach as powder synthesis and layer fabrication are combined in one step.

The top XRD pattern in Figure 4 from a Sr-doped LaMnO₃ cathode layer deposited on a 8YSZ substrate in the LRD™-200 reactor and subsequently fired at 1100°C for 1 hour. The XRD at the bottom is that of the 8YSZ substrate. A comparison of the two patterns shows that the only new peaks observed in the deposited layer are from LSM. There is no indication in the XRD pattern of the LSM layer that the insulating phase La₂Zr₂O₇ has formed. The broad peaks for the LSM phase are indicative of small particle size even though the layer was exposed to high temperatures. A rough estimate shows the average crystallite size is 55 nm. The SEM micrograph shown in Figure 5(a) reveals spherical morphology and small particle size whereas the micrograph in Figure 5(b), taken from a cathode layer fabricated in the same LRD™ run but subsequently fired at 1200°C for 1 hour, shows an interconnected structure. The SEM analysis showed both microstructures possess a suitable degree of porosity with a distribution of pore sizes from less than 1 μm to near 10 μm.

The results described above demonstrate the potential of using LRD™ technology to fabricate high quality SOFC cells. Directly converting metal precursors into SOFC layers in the LRD™ reactor eliminates the need to undertake powder synthesis, calcining,
ball milling, batch formulation, slurry preparation, tape formation, and binder burnout steps required in conventional SOFC cell fabrication. Figure 6a compares LRD™-based cell manufacturing with conventional cell manufacturing technology. With LRD™ processing, the number of steps is reduced by more than 50%. Additionally, the build up of SOFC layers using LRD™ technology is accomplished without solvent carriers or organic binders, eliminating the slow drying and binder burnout steps and the deposition can be tailored to yield layers at or close to the final desired density. This has a number of advantages. First, the total cycle time from raw material to finished cell is reduced from days or weeks to hours. Secondly, the effect of powder morphology on layer formation is essentially eliminated, providing greater freedom in optimizing performance and also allowing incorporation of high surface area nanomaterials. Thirdly, hazardous binder effluent streams are eliminated to create a “green manufacturing” approach for these green energy generation devices. In addition to the process advantages, the number of individual pieces of equipment required to fabricate a cell is reduced by more than 50% as compared to conventional, tape-based processes. Furthermore, the raw material considerations are greatly simplified as shown in Figure 6b as over 80% of the raw material variables and 75% of the raw material suppliers are eliminated.

Various types of deposition technologies have been demonstrated for SOFC fabrication such as plasma spray, combustion flame spray, and physical vapor deposition. Though these approaches have their merits, the LRD™ route has several attributes that make it superior to other deposition methods; pre-synthesized and spray-dried powders or pre-fabricated targets are not required, low cost process gases can be used, a linear deposition plume is generated, and porosity can be engineered through reactor settings. These attributes provide more versatility for component development, higher throughput, increased uniformity, and lower cost. Additionally, the nature of LRD™ deposition and translation combined with its direct conversion of chemical precursors makes this approach ideally suited to creating electrodes with a gradient in electrocatalyst content along the fuel or oxidant flow direction. This will yield increased thermal uniformity across the cell during operation, increasing stack durability and reactant utilization, while reducing system capital and operational cost. Furthermore, binder burnout and sintering shrinkages are either eliminated or reduced significantly, reducing cell warping. Flatter cells simplify sealing leading to improved stack durability. Lastly, LRD™ technology provides an avenue for fabricating advanced cell and stack designs such as metal-supported cells for APU and backup power applications where rapid thermal ramping is required.

The advantages of LRD™ technology can also be leveraged in the fabrication of other stack components such as interconnects, seals, and current collectors. Protective layers for inexpensive stainless steels can be applied to achieve costs below target without sacrificing durability. High quality sealing materials can be directly applied to select areas of cells, interconnects, and/or frames. Low-cost metal oxide current collectors can be developed and manufactured using LRD™ processing. Therefore, LRD™ technology can provide the backbone of SOFC stack manufacturing.

The high degree of versatility makes LRD™ processing well suited to cost-effective development of stacks and stack components. Scale-up from lab demo to pilot-plant to volume manufacturing, on a m²-component/hr basis, is linear as it can be achieved by extending the LRZ and reactant plume along the nozzle axis. Accomplishing this is a
matter of engineering proper photon density and fluid dynamics, a much more tractable task than managing the quality and yield when scaling the multiple unit processes of powder and tape-based manufacturing (Figure 6a, bottom). The linear scalability plus the comparative simplicity of LRD™ processing (as exemplified in Figure 6) allow a modular approach to be applied to building production capacity. This modularity makes LRD™ technology suitable for low cost manufacturing of SOFC stacks and components at low volumes necessary for initial market development. An illustrative stack manufacturing scheme using LRD™ technology is shown in Figure 7. Multiple LRD™ reactors are connected forming a manufacturing line to sequentially deposit the necessary layers for fabricating cells along one line (upper) while another line (lower) deposits protective coatings on either side of low-cost metal plates followed by deposition of sealing material. These components are then assembled into a stack using a robotic tool and finally cured to finish the stack.

![Figure 6. Comparison of LRD™ manufacturing route with conventional routes for (a) SOFC cell manufacturing and (b) SOFC process supply chain.](image)

Cost has been raised as a concern for laser-based processing methods. Detailed manufacturing models have been constructed for LRD™ processing and used to perform extensive cost analysis for SOFC manufacturing. This analysis takes into account chemical precursor consumption, process gases, capital cost of laser and deposition equipment, labor, facilities, and other factors associated with fabricating a complete multilayer SOFC cell. Industrial CO₂ lasers used in LRD™ technology are high-reliability, high efficiency models used in a variety of high volume manufacturing processes, including automotive. The use of an absorber with an absorption line at the same frequency as the laser source creates a high optical to thermal efficiency that,
combined with high wall-plug efficiency CO₂ lasers (5.4%, including required chiller), yield competitive manufacturing costs for Si₃N₄ and SiC powder (18). Karakoussis et al. recently calculated the total energy input for materials and manufacturing SOFCs via the conventional approach (combined tape-casting and screen-printing) at 248 MJ\textsubscript{energy}/KW\textsubscript{SOFC} (5). In comparison, an LRD™ line (as shown in Figure 7, top) producing similar cells in high volume and comprising multiple lasers would reduce total energy input by approximately 50%. The energy savings is realized because the LRD™ process combines powder and layer synthesis into one step to dramatically reduce the number of unit processes (see Figure 6a). To determine manufacturing cost, vendor quotes for precursors and equipment as well as actual labor, utility, and facility costs for a manufacturing location in the Western United States were used. This analysis has shown that for a multi-layered anode-supported cell, the costs for laser operation, process gases, and aerosol solvent be approximately 10 to 12% of a total manufacturing cost that is significantly lower than forecasts for conventional processes (4). Furthermore, it was found that in addition to replacing 66% of the steps and 50% of the equipment in conventional processing and eliminating vendors for powder and process organics (see Figures 6 and 7), the LRD™ approach reduces sintering capital and operational costs by 50 to 75%. The efficiency of the process combines with the fact that the LRD™ reactor replaces powder synthesis, modification, batching, and fabrication equipment to yield SOFC stack manufacturing costs that are as low as 50% of the DOE-SECA 2010 targets (19) at substantially lower manufacturing volumes.

**CONCLUSIONS**

Laser Reactive Deposition is a novel economical method for fabricating Solid Oxide Fuel Cells. Preliminary results have shown that simple chemical precursors can be combined in solution and transformed into SOFC layers. The layers fabricated on 8YSZ substrates using the LRD™ approach are of the desired phase with crystallite sizes in the nanoscale region, even after sintering at high temperatures. The composition and phase content of the deposited layers can be readily adjusted by altering the feedstock metal precursor ratio. Electrodes produced using LRD™-technology are expected to have high triple-

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**Figure 7.** Example scheme for manufacturing SOFC stacks using LRD™ technology. The six manufacturing steps based on LRD™ reactors are shown in bold lines.
phase boundary region. The high reaction zone temperatures of the LRD™ process creates microstructures that are expected to be thermally robust at SOFC operating temperatures, a requirement for satisfactory durability of cells and interconnect protective layers.

The inherent efficiency of the LRD™ process due to its ability to directly convert chemical precursors into SOFC layers, provides several advantages. Manufacturing cost targets can be achieved at production volumes consistent with early market levels, scale-up of size and throughput is significantly simplified, and development cycles for new components and/or new materials are dramatically compressed. These attributes will enable the mass commercialization of SOFC systems.

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