Protective Ceramic Coatings for Solid Oxide Fuel Cell (SOFC) Balance-of-Plant Components

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ABSTRACT

Solid oxide fuel cells (SOFCs) can extend the nation's energy reserves. SOFC materials must ensure safe, reliable and continuous operation for 10 years in harsh operating conditions to fully harness this clean energy source.

In a prior SBIR Phase I Grant from DOE (DE-SC0011286), InnoSense LLC (ISL) developed and evaluated yttria-stabilized-zirconia (YSZ) coating formulations to serve as bonding surfaces for compliant glasses used in SOFC interconnect seals.

In this work, the company:

1. **demonstrated processes and materials on 430 SS/ 441 SS test plaques to fabricate SOFC cell/interconnect plate sheet flow channels for the cathode-side air and anode-side fuel,**
2. **tested initial YSZ coatings' potential for near-hermetic sealing, and**
3. **estimated production costs to achieve targeted industry goals.**

Building on our YSZ coating formulation, ISL is developing low-cost barrier layer coatings for SOFC balance of plant (BOP) components. The barrier coating will serve two functions:

1. **isolate the BOP component surface from the hot humid gases within the SOFC facility and**
2. **eliminate or minimize the chromium (Cr) species evolution at 700 – 900 °C that can poison SOFC cathodes and degrade electrochemical performance.**

ISL is developing low-cost coatings of refractory ceramics such as YSZ and Al_2O_3 using modified sol-gel formulations. These coatings will be applied to cathode-side hot piping and/or heat exchangers by low-cost processes such as dip coating.

The company is developing low-cost dip coatings for interior surfaces (piping with joint welds, baffles, etc.) and irregular geometries in order to mitigate Cr volatility as effectively as industrial pack cementation and vapor coatings.

These coatings will be deposited onto substrates of known SOFC materials such as 430 and 441 SS. Our collaborators at UConn will perform microstructure analysis. They will also carry out Cr transpiration testing (to generate Cr vapors for quantitative analysis), thermal cycling (to determine the duration for oxygen resistance), and 3D X-Ray tomography. The success of the coating will represent an important step toward expanding the capabilities of SOFCs to a 10 year lifetime to become competitive with fossil fuel burning conventional electrical power plants.

BACKGROUND AND TECHNICAL APPROACH

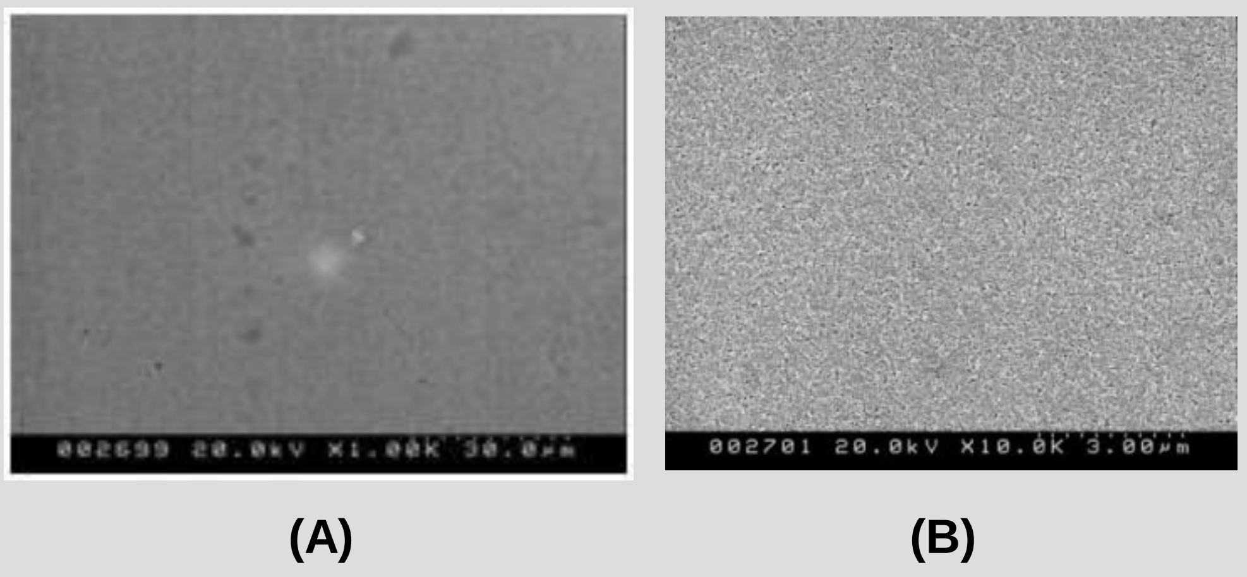
RESULTS FROM PREVIOUS WORK

SOFC cost is reduced by using ferritic stainless steel such as 441 SS rather than costly ceramic conductive elements. Cracks, however, can occur in SOFCs. *Recent developments of compliant glasses have addressed seal cracking, but these glasses interact with the stainless steel conductive elements. A thin, 1–2 µm, adherent Yttria Stabilized Zirconia (YSZ) coating can act as a diffusion barrier, but must be applied to shapes like a square annulus and be economical.*

In a previous DOE sponsored project, ISL was developing a YSZ metallo-organic based screen printable ink system. The ink is a modified sol-gel formulation. Since good printing inks require thixotropic rheology to induce leveling and prevent edge flow, a thixotropic agent was included. A stress relief agent was incorporated into the formulation to relieve stresses that would otherwise result in crack propagation in the films upon drying.

ISL is developing sprayable and screen printable formulations:

- **Fired in air or controlled atmosphere**
- **Fired on stainless steel**



(A) **(B)**

Figure 1
Dried single thick film coating with no drying cracks even at high magnification **(A)** 1,000X and **(B)** 10,000X.

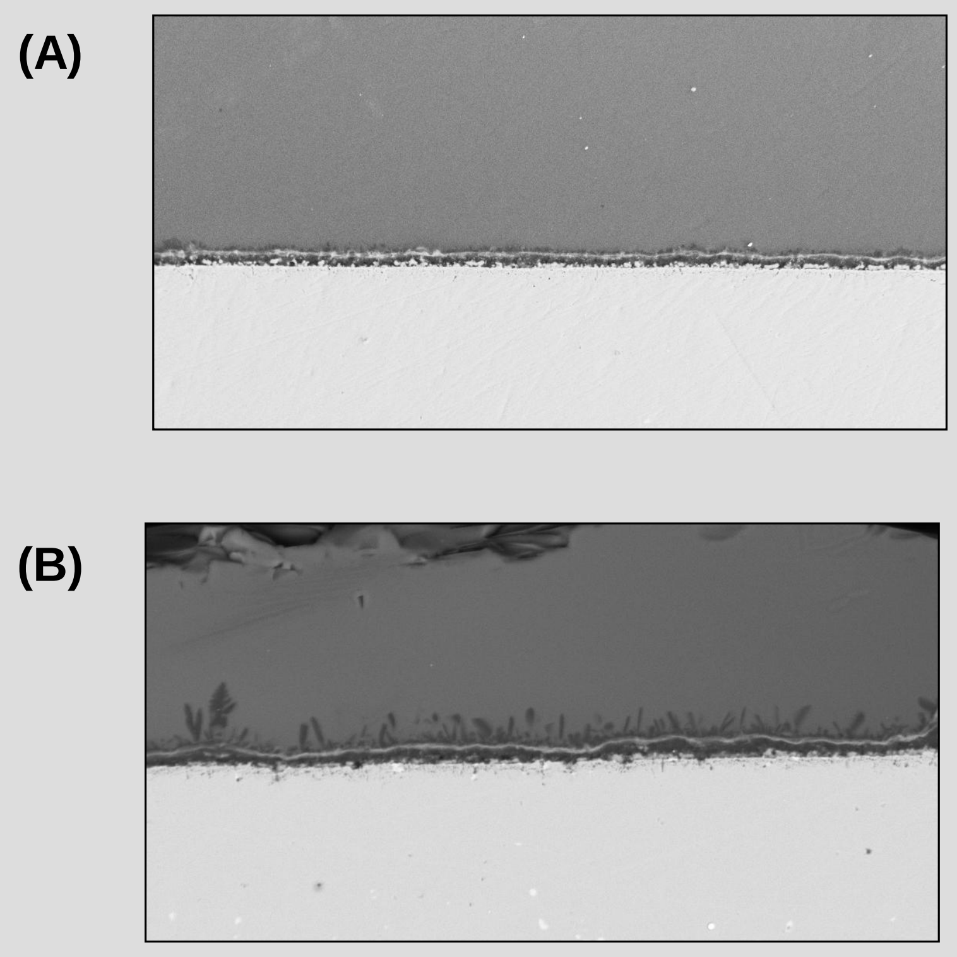


Figure 2. For both photomicrographs, the layers shown include: from bottom to top: 441 SS substrate (bottom layer), spinel, YSZ coating, and SNC glass (top layer). The effect of time (same samples, different treatment time): A7-Z-G (135 h) **(A)** and B7-Z-G (294 h) **(B)**. This is not an easy comparison since samples are not uniformly affected. Here, reasonably good regions of two samples are compared. The conclusion is that glass attack of the interconnects increases with time.

DIP COATING METHOD

Dip coating techniques are processes where a substrate is immersed in a fluid and then withdrawn with a well-defined withdrawal speed, controlled temperature and atmospheric conditions.

The coating thickness is mainly defined by the withdrawal speed, solid content, and liquid viscosity.

If sheer withdrawal speed rates keep the system Newtonian (relatively slow), then the coating thickness is described by the Landau-Levich equation[1,2,3]:

$$h = 0.945\ \alpha \times \text{capillary length} \times \text{capillary number}$$

$$= 0.945\ (\eta v)^{2/3} / [\ \gamma^{1/6}\ (\rho g)^{1/2}\ ]$$

where:

α = thickening factor, h = coating thickness, η = viscosity, γ_{LV} = liquid-vapor surface tension, ρ = density, g = gravity.

For classic acid catalyzed silicate sols, thicknesses obtained experimentally fit well to calculated values. For dip coating, by choosing an appropriate viscosity, the coating thickness can be varied with high precision from 20 nm - 50 µm.

For reactive systems like sol-gels using alkoxides or pre-hydrolyzed systems, control of the atmosphere is paramount. The atmospheric properties control solvent evaporation and the subsequent sol destabilization by solvent evaporation, leads to gelation, and the formation of a transparent film due to the small particle size in the sols.

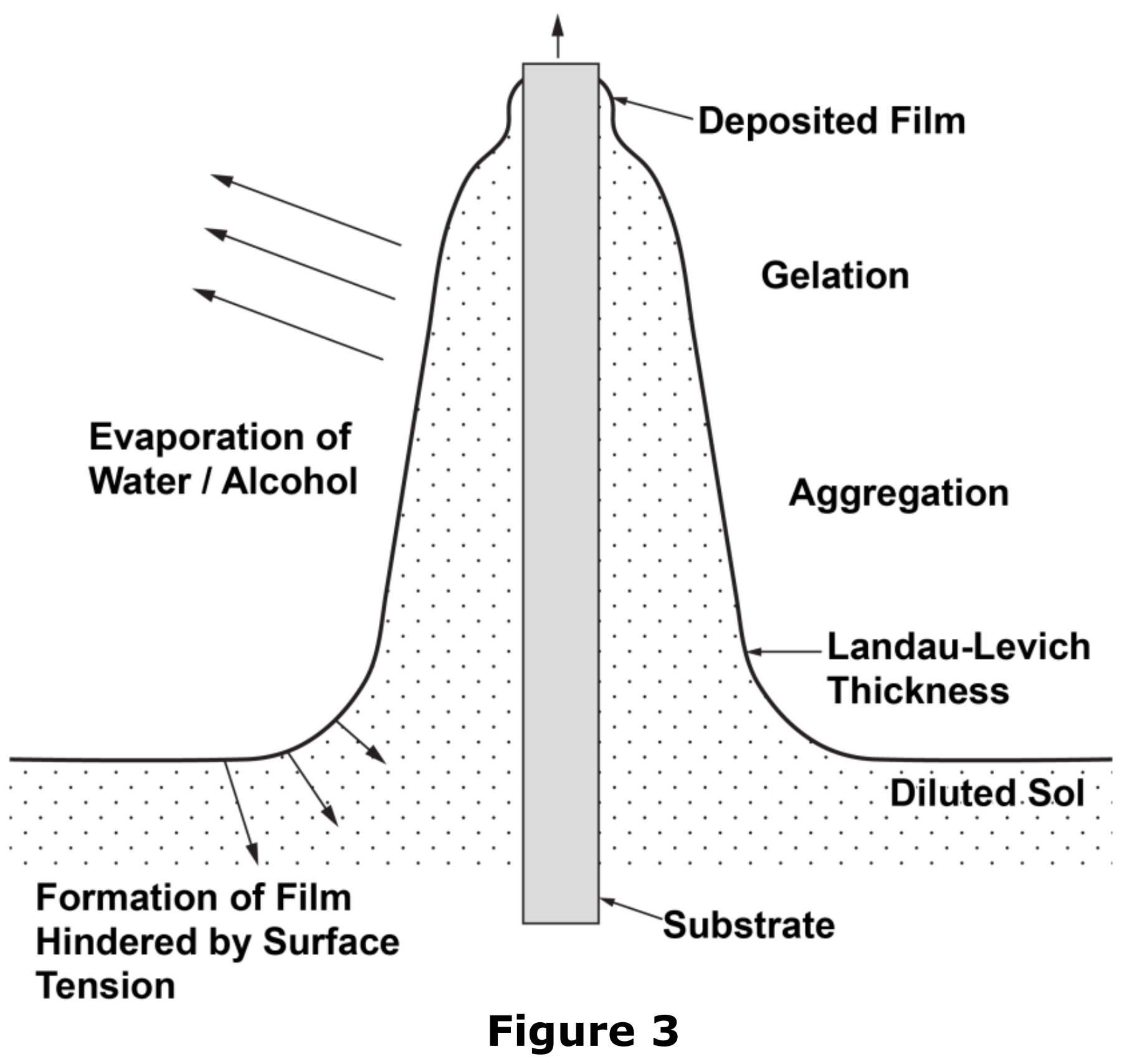


Figure 3
Drying process during dip coating from sol-gel to deposited film. Note the Landau-Levich equation gives an estimate of thickness[1].

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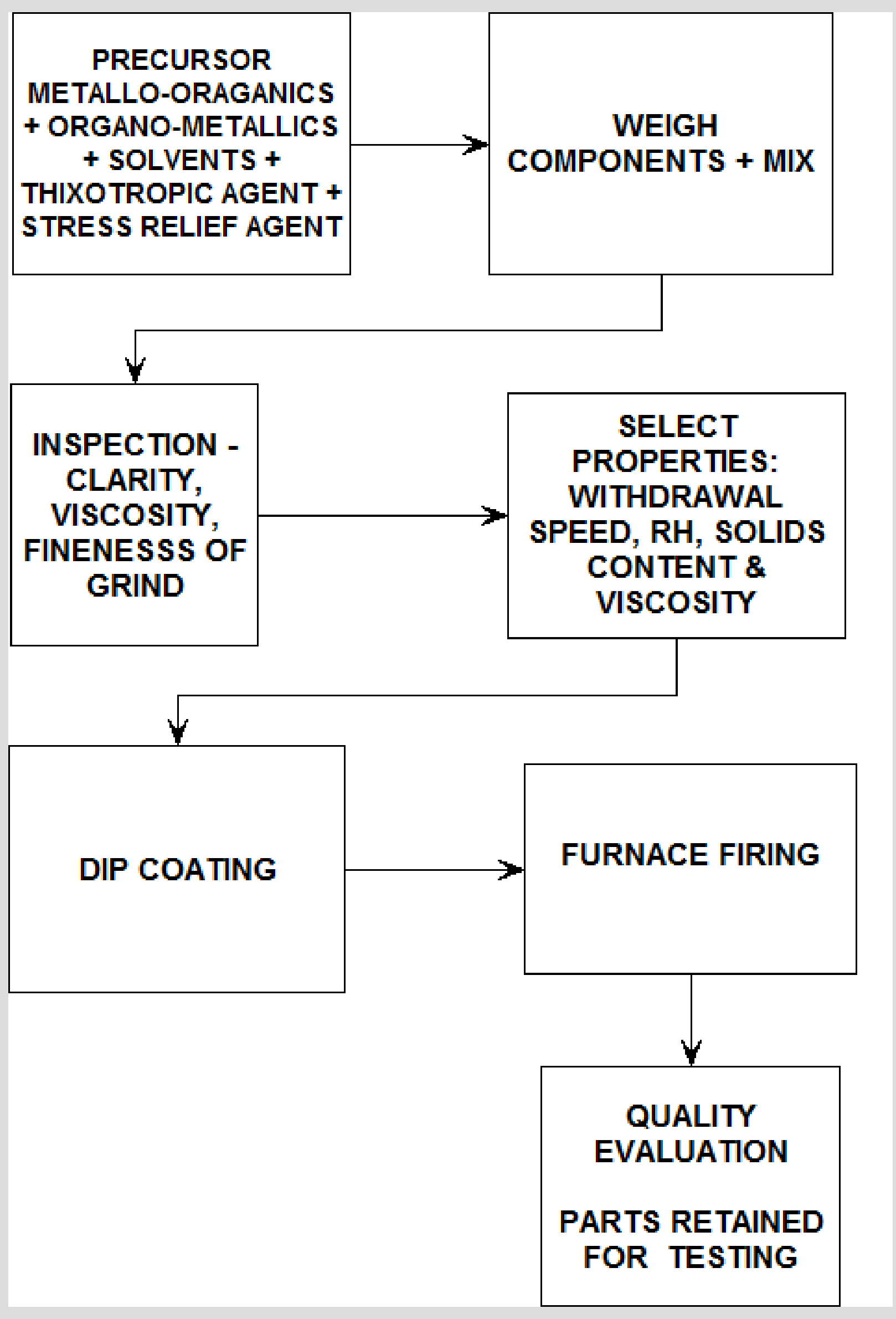
3. Mayer, H. C. and Krechetnikov, R. "Landau-Levich flow visualization: Revealing the flow topology responsible for the film thickening phenomena." *Physics of Fluids* 24, **2012**, 052103.

DIP COATING METHOD


PRECURSOR METALLO-ORAGANICS + ORGANO-METALLICS + SOLVENTS + THIXOTROPIC AGENT + STRESS RELIEF AGENT
WEIGH COMPONENTS + MIX
INSPECTION - CLARITY, VISCOSITY, FINENESSS OF GRIND
SELECT PROPERTIES: WITHDRAWAL SPEED, RH, SOLIDS CONTENT & VISCOSITY
DIP COATING
FURNACE FIRING
QUALITY EVALUATION

PARTS RETAINED FOR TESTING

Figure 4
Flow chart for dipping operation using modified sol-gel.


(A) **(B)**

Figure 5.
CNC driven custom dip coater. **(A)** 1321 Axis Slide, 13 inch Stepper Motor & Mount, CNC Linear Controller. **(B)** Set up as a dip coater for samples to be moved into and out of the fluid with controlled speed.

PROJECT SCHEDULE AND MILESTONES

PHASE I PROJECT TASKS, TIMELINE AND MILESTONES

The major tasks and milestones for Phase I are being accomplished in accordance with the schedule shown in Figure 6.

	Tasks	Target Completion Date	Task Status	Months After Project Initiation								
				1	2	3	4	5	6	7	8	9
1	Project Implementation and Management	6/30/2015	Complete	▨								
2	Acquire Material and Equipment.	7/31/2015	In Progress	▨	▨							
3	Develop Chemistry to Achieve Uniform Dip Coat Deposition.	11/30/2015	In Progress		▨	▨	▨	▨				
4	Define Surface Roughness Specification	11/30/2015	In Progress		▨	▨	▨	▨				
Milestone 1: Achieved YSZ for uniform and continuous dip coating.								▨				
5	Perform Testing	3/08/2016	In Progress					▨	▨	▨	▨	▨
Milestone 2: Produced a range of dipping paints or inks / process settings to produce continuous 1 to 2 µm fired film thicknesses.									▨			
Milestone 3: Completed ISL and UConn testing.												▨
6	Evaluate the Product's Commercial Potential.	3/08/2016	In Progress		▨	▨	▨	▨	▨	▨	▨	▨
7	Submit Reports.	3/08/2016	In Progress									▨
Milestone 4: Project successfully completed and grant obligations met.												▨

Figure 6
Research Program Schedule for Phase I**.**

WORK ACCOMPLISHED TO DATE

- **Previous formulations have been developed for both screen printing and spray application.**
- **Initial problems with precipitation of YSZ were eliminated, with inks stable at least for 2-3 months.**
- **A thixotropic additive was successfully incorporated into the formulation, along with a stress relief agent to eliminate drying cracks.**

Acknowledgment
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