Effect of Solution Chemistry on Coating Microstructure by Solution Precursor Plasma Spraying

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***Abstract*:** Solution Precursor Plasma Spray (SPPS) is a thermal spraying process that uses a thermal plasma as the heat source and aqueous solutions as the feedstock. SPPS has demonstrated the potential to produce as-deposited coatings comprised of nano-size particles agglomerated into porous spheres with interconnected pores between spheres for SnO_2 coatings. These coatings could be advantageous as electrochemical electrodes for gas sensors**.** This paper discusses the fabrication of as-deposited porous $LiFePO_4$ coatings, of interest as electrodes for battery applications. Different solution chemistries were used to produce a reducing environment for deposition. Solution precursors containing lithium ions, iron ions with phosphoric and phosphorous acids were compared. The microstructures and morphologies of the coatings were examined by SEM and XRD. The results show effects of solution chemistry on the substrate temperature during deposition, and on the phase composition and porosity of the deposit.

Introduction

Solution Precursor Plasma Spraying (SPPS) is a plasma thermal spraying process using solution precursor feedstock mixed at the molecular level and injected into the high temperature plasma jet. The plasma jet evaporates solvent, precipitates/pyrolyzes solute into solid particles and further melts the particles before arriving on a substrate. Depending on the solution concentration and size of droplet formed inside the plasma, different types of precipitation are dominant (volume or surface precipitation). Further heating of these different types of precipitate leads to molten splats, solid particles and hollow/fragmented shells (1). Dense coatings could be formed by over-lapping of molten splats. The hollow/fractured shell deposit gives porous coatings. The combinations of different types of particles that arrive on the substrate determine the final microstructure and therefore the properties (2). The unique microstructures of these deposits make SPPS an emerging deposition process with capacity to deposit dense to porous ceramic coatings. This paper focuses on the effect of solution chemistry for SPPS spraying on the coating microstructure.

Experimental Procedure

Preparation of Solution and Spray Set-up

The solution precursors were prepared by dissolving $LiNO_3$, $Fe_2(NO_3)_3$ and two phosphorus acids into water at 1:1:1 ratio. Phosphoric and phosphorous acids were used. Both precursor solutions were further modified by addition of 5 wt% of sucrose. As Figure 1 illustrates, all four solution precursors were injected as a stream by the EFD Microspray™ valve 2 mm downstream of the plasma gun exit and 15 mm below the plasma centerline. The operating parameters of plasma torch are provided in Table I. All solution precursors were deposited on 304 stainless steel substrates at 50mm spraying distance. The deposition time was 90 seconds with 16 passes.

Plasma			**Solution**	
Power	CO_2+CH_4	Ar	Nozzle	Flow rate
36Kw	28 SLM	10 SLM	200μm	23ml/min

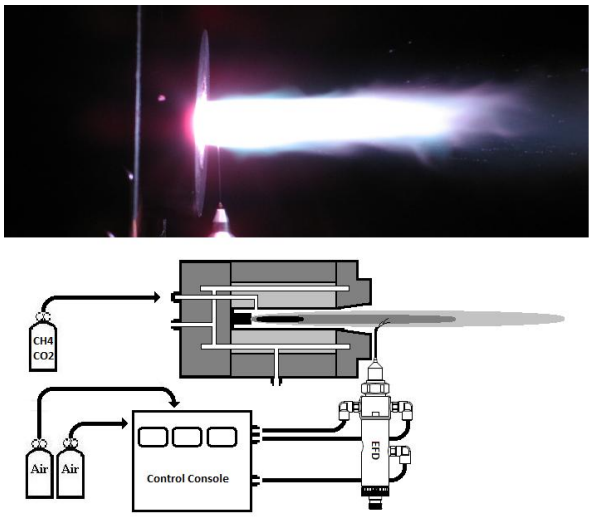

Figure1: *Schematic drawing of solution injection and position of the injector*

Coating Characterization

The coating morphologies were studied using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray spectroscopy (EDS) for elemental analysis. The as-deposited crystal phase was examined with copper K_α X-ray diffraction (XRD). The relative porosities of the coatings were calculated from polished cross-sections by CLEMEX image analysis software.

Results

The XRD results show all four solution precursors have $Li_3Fe_2(PO_4)_3$ as the major phase in the as-deposited coatings. The XRD results imply the final coating phase is insensitive to different phosphorus acids and addition of sucrose. Figures 2a and 2b show the morphologies of coatings from phosphorous and phosphoric acid solutions respectively. There is no discernable morphology difference between the solution precursors. Both coatings show typical SPPS deposits with particle size in 2-5 µm range and some fragmented shells. The calculated relative porosity of the coatings are 36.2±8%.

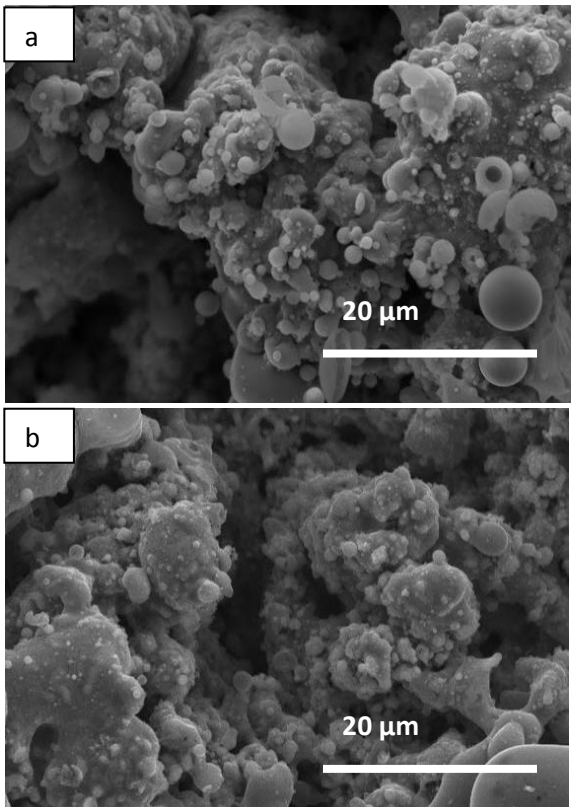

Figure 2: *the as-deposit coating morphologies for both acids.*

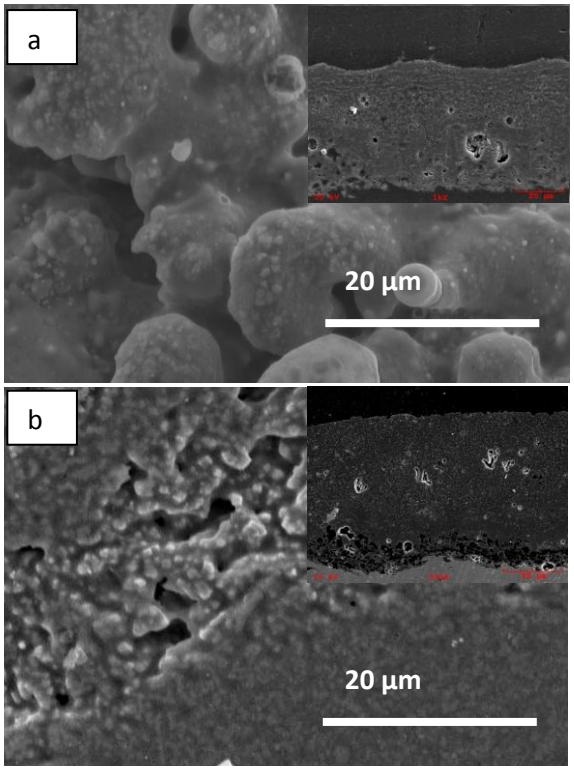

Figure 3*: the effect of sucrose on morphologies of both coatings***.**

Figures 3a and 3b depict the effect of 5 wt% sucrose in phosphorous and phosphoric acids solution precursor. As it can be seen in the figures and the inserts, the coatings are dense with a thickness of about 150µm with some embedded pores in the range of 5-10µm. The calculated relative porosity is 7.2±2.3%.

Discussion

The substrate temperatures for all coatings were monitored with K-type thermocouples at the back of the substrates during deposition. Figure 4 summarizes the temperature profiles during deposition with various solution precursors. The final temperatures for phosphorous acid solutions with/without sucrose and phosphoric solutions with/without sucrose are 600/525 and 400/350 degrees Celsius, respectively. The profiles show the addition of sucrose raises the substrate temperatures 25-75 degree higher for both solution precursors. It is known sucrose serves multiple purposes in the solution combustion synthesis process. The sucrose serves as extra fuel and also as a dispersing agent to promote nucleation (3). The sucrose has a fuel and oxidizer ratio of 1.53 (5). The combustion reaction is fuel lean and provides a minor increase in enthalpy. The minor increase in substrate temperatures for both solution precursors are attributed to the additional combustion provided by sucrose in SPPS.

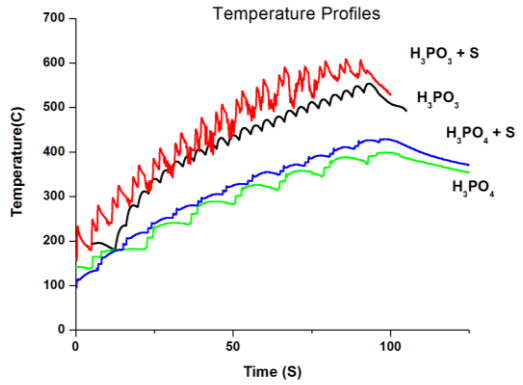

Figure 4*: temperature profiles for all four precursors.*

It is observed that the temperature of the phosphorous acid precursor solution is about 200 degrees higher than the phosphoric acid solution precursor. The phosphorous acid thermally decomposes to release hydrogen in the presence of water (4). The combustion of the hydrogen supplies extra enthalpy and results in higher substrate temperatures.

Despite the fact of higher enthalpy from hydrogen combustion for the phosphorous acid solution precursor, the phosphorous and phosphoric acid solution precursor coatings are both porous without the sucrose addition. The increase of enthalpy alone therefore does not explain the formation of dense coatings with sucrose. In fact, the dense coatings are comprised of partially molten nano-particle aggregates in the range of 100 nm as shown in figure 5. It is postulated the addition of sucrose affects the sequence of precipitation and pyrolysis routes.

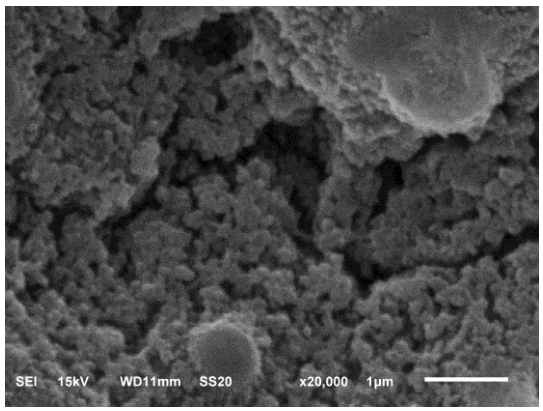

Figure 5*: nano-particle aggregates on the coating surface*.

It is known that addition of sucrose promotes formation of an intermediate gel precursor phase due to high viscosity. The oxide nucleates and crystallizes from the gel phase. The pyrolysis route for a sucrose solution precursor explains the unique hollow shell in figure 6. As soon as the solution is broken up into ~20 µm droplets, water rapidly evaporates away from droplet surface, and a viscous gel crust forms. The gel

crust then decomposes into the oxide accompanied with release of off-gas.

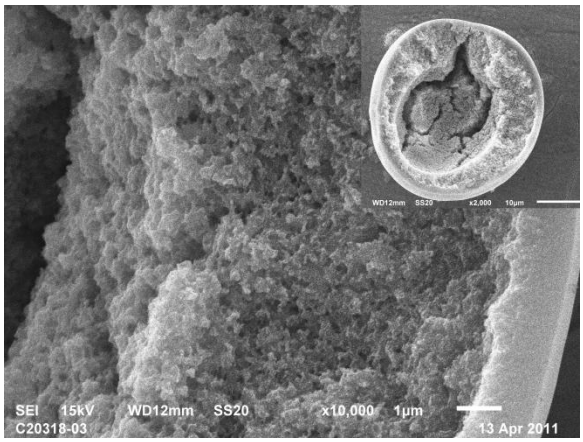

Figure 6*: a fractured hollow sphere consists of nano-particles***.**

The insert on the top right corner of figure 6 indicates the thickness of the shell is around 10μm and the interior of the shell is porous with aggregates of nano-particles. The outer surface of the shell is a dense impermeable layer around 1μm thick and can cause pressure build-up and fracture.

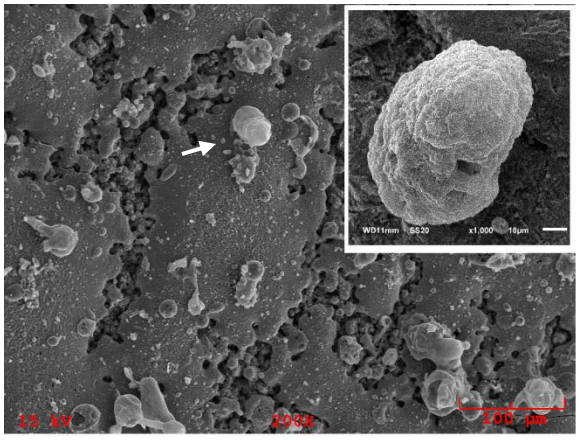

Figure 7: *hollow sphere on the dense coating*

The results and findings suggest the addition of sucrose and intermediate gel phase combustion alters the precipitation and pyrolysis routes of solution precursor during deposition. The formation of a gel phase could delay the pyrolysis, therefore the hollow/gel phase particle arrives on substrate. Subsequent passes of plasma tails melts and sinters the nano-particles into dense coatings. Figure 7 reveals some un-decomposed gel phase, indicated by the arrow, on the dense coating. The insert shows a close up of the hollow sphere.

Conclusion

Four different precursor solutions were injected into the plasma jet. The solution precursors containing sucrose resulted in dense coatings comprised of nano-particles. The morphologies of the coatings and substrate temperatures suggest the addition of sucrose alters the SPPS deposition mechanism and promotes the nucleation of nanoparticles.

References

1. *Fluid Mechanics and Heat Transfer of Liquid Precursor Droplets Injected into High-Temperature Plasmas.* **Saptarshi Basu, Eric Jordan, Baki Cetegen.** 2008, Journal of Thermal Spray Technology, pp. 60-72.

2. *Formation of Vertical Cracks in Solution-Precursor Plasma-Sprayed Thermal Barrier Coatins.* **Liangde Xie, Dianying Chen, Eric Jordan, Alper Ozturk, Fand Wu, Xinqing Ma, Baki Cetegen, Maurice Gell.** 2006, Surface and Coatings Technology.

3. *Mass Production of LiFePO4/C Powders by Large Type Spray Pyrolysis Aparatus and Its Application to Cathode for Lithium Ion Battery.* **Shinsuke Akao, motofumi Yamada, Takayuki Kodera and Takashi Ogihara.** 1, s.l. : International Journal of Chemical Engineering, 2010, Vol. 2010. 5.

4. **Corbridge, D.E.C.** *Phosphorus.* New York : Elsevier Scientific , 1980.

5. *A Novel Preparation Method of Active Materials for the Lithium Secondary Battery.* **Seung-Beob Yi, Hoon-Taek Chung, Ho-Gi Kim.** s.l. : Electrochemistry Communications, 2007, Vol. 9. 591-595.