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Suspension Plasma Spaying of Intermediate Temperature SOFC Components using an Axial Injection DC Torch

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Abstract. Intermediate temperature SOFC components, such as dense, nanostructured SDC electrolytes (samarium doped ceria) and porous anode sublayers were fabricated by suspension plasma spraying using an axial feed dc plasma torch. The liquid carrier employed in this approach allowed for controlled injection of much finer particles than in conventional thermal spraying, leading to thin coatings with a refined microstructure. Dense, thin (<10μm) and non-fractured electrolytes were created. Various processing routes for SOFC half-cells, using tape-cased, plasma-sprayed and suspension-sprayed anodes, were explored. Loss of integrity and non-continuous coverage of the anode constituted the principal difficulties in the subsequent electrolyte deposition. The role of suspension feedstock particle size is discussed. Amongst various schemes investigated, a processing route that employs sequential suspension plasma spraying steps for both the electrolyte and the anode, using relatively large primary particles in the feedstock, constituted the most promising approach.

Introduction

Solid Oxide Fuel Cells (SOFC) produce electrical energy directly from hydrogen and hydrocarbon gaseous fuel. As compared to conventional power generation systems, these cells have high conversion efficiencies and bear a low environmental impact.

A key issue for commercialization of next-generation SOFCs is the reduction of component and overall manufacturing costs. Traditional SOFCs, using zirconia (YSZ) electrolyte systems, operate at elevated temperatures of 900-1000°C. Using ceria-based electrolytes, such as samarium doped ceria (SDC), equivalent ionic conductivity can be attained at much lower temperature (600°C) [1-4]. A lower or intermediate operating temperature (IT) can drastically reduce the material cost of the overall cell, since more economical and robust metallic interconnect and support/insulation components can be used.

Air plasma spraying (APS), an established and universal industrial process, is a promising and cost-effective technique for the manufacture of SOFC units [5,6]. Multiple SOFC components, including the electrodes and the electrolyte, could be produced sequentially and directly on a metallic interconnect substrate with a single deposition technique, thereby minimizing the number of processing steps and equipment required [6]. In particular, the high temperature sintering steps required in many other layer deposition techniques could be eliminated. To realize the potential of the new IT-SOFC technology, a thin, nanocrystalline and gas-tight electrolyte layer is essential to separate the fuel from the oxidant atmosphere [1]. Conventional thermal spraying is, however, limited to large feedstock powder (10-100μm) and consequently to large coating thicknesses between tens to hundreds of microns.

Suspension plasma spraying (SPS) using a liquid feedstock carrier is an emerging technology that permits the projection of much finer starting powder and allows the formation of thinner coatings. In this process a feed suspension is injected directly into the plasma flame. The plasma-liquid interaction atomizes the suspension into a fine mist and evaporates the suspension medium, thereby concentrating the solid content into micro-sized particles. The small particles are then nearly immediately accelerated to the plasma gas velocity. At impact on the substrate, these particles form thinner lamellae with rapid solidification rates. Thin coatings (3-20 μm) with a more refined microstructure and grain size than in conventional thermal spraying are thereby created [7,8].

In this study, the suspension feedstock is axially injected into the center of three converging plasma streams of a Mettech Axial III plasma torch (Northwest Mettech Corp., Richmond, BC, Canada). This technique is illustrated for consolidating dense and nanostructured SDC electrolyte coatings. Potential processing routes for IT-SOFC manufacturing, which include electrolyte deposition on porous tape-casted NiO-YSZ anodes, on metal-supported plasma-sprayed NiO-YSZ and suspension-plasma-sprayed NiO-SDC are explored. Prior to spraying an assembled half-cell (interconnect-anode-electrolyte) system, the coatings were produced individually for optimized torch operating and feed conditions.

Experimental Details

The suspension spraying system used for SDC electrolyte and NiO-SDC anode production employed a Mettech Axial III torch equipped with an internal injection/atomization module, using nitrogen as atomizing gas. Typical torch operating conditions employed in this study are summarized in Table 1.

Table 1: Operating Conditions (Mettech Axial III)

Cond.	Torch current X3	Gas Flow (slpm)	Ar %	N_2 %	H_2 %	Power (kW)
1	180 A	180	45	45	10	85
2	200 A	245	75	10	15	83
3	200 A	275	75	15	10	90

In-flight particle states were measured with a commercial diagnostic system (Accura-Spray ® G2 Tecnar, St-Bruno, PQ Canada). The temperature measurement is based on two-colour pyrometry, and the velocity is determined by a time-of-flight technique. The measurement volume was centered in the spray plume at the location of the substrate during deposition i.e., at 50 mm and 62.5 mm [7]. Measurement of in-flight particle velocity and temperature of ceria containing materials was impeded by strong evaporation and optical transparency at high temperatures [9]. Based on measurements of zirconia nano-particle suspensions at the same spray conditions, an indirect approach to rank the in-flight particle states for each set of spray parameters was adopted. Zirconia was chosen as model material, since its melting point (2715°C) is close to the ceria ceramic mixture (2600°C). Conventional plasma spraying, using a MB-F4 plasma torch (Sulzer Metco, Westbury, NY, USA), was employed for the production of nickel-oxide / yttria stabized zirconia (NiO-YSZ) anode coatings. In-flight particle states were monitored with a DPV 2000 diagnostic tool (Tecnar Automation, St-Bruno, PQ Canada).

Microstructures were observed by SEM (JEOL JSM-610) and FE-SEM (Hitachi S4700) on the cross-section of a polished sample. Standard metallographic preparation methods were used. Porosity was assessed on the cross-section by SEM (1000 X), using image analysis. The intensity range and thresholds were standardized on reference materials, and five measurements were averaged per sample. Phase analysis was carried out by XRD using a Brucker D8-Discovery diffractometer with Cu-K_{α} radiation at an acquisition of 0.01°/sec. The Sherrer method was used to estimate the crystallite size of the coatings. Suspension of 5 wt% solids in ethanol were prepared for samarium doped ceria ($Sm_{0.2}Ce_{0.8}O_{1.9-x}$) (20 nm, SSA 220 m^2/g) (nGimat, Atlanta, GA, USA) for the electrolyte and 10 wt% NiO:SDC (50/50wt%) for the anode material. To prevent sedimentation during processing, the suspensions were stabilized with polyethyleneimine (PEI) (MWT 25,0000, Alfa Aesar, USA), acting as a cationic polyelectrolyte dispersing agent. The dispersant concentration and pH were optimized using sedimentation tests. Two different feedstock powders for the anode material were tested: NiO:SDC with a primary particle size of 20 nm and a nominal

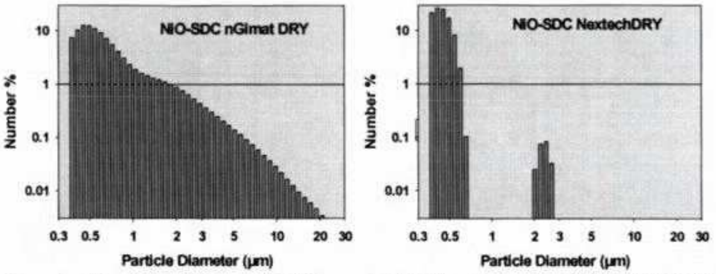

Fig. 1: Particle Size of NG and NT feedstocks (NiO-SDC)

surface area of 200 m^2/g (nGimat, Atlanta, GA, USA) (NG), as well as a larger NiO:SDC powder with nominal particle size of 4.71 µm and a specific surface area of 1.2069 m^2/g (Nextech Materials, Lewis Center, OH, USA) (NT). Particle sizes were measured with a Coulter LS Particle size analyzer and are shown in Fig. 1. The wide particle distribution of the NG powder reflects the loose agglomerates of very fine primary nano-particles. On the other hand, the bimodal distribution of the NT powder distinguishes the smaller SDC and the larger NiO particles in the mixture. Zirconia based anodes were produced from an agglomerated and sintered nanostructured thermal spray powder of 50 wt% NiO (APS 20-50nm) and 50 wt% YSZ (8% Yttria) (APS 40-60 nm) with an average granule size of 30-40 µm (Inframat., Willington, CT, USA).

Results and Discussion

Electrolyte Layer The microstructure of samarium doped ceria coatings deposited on a solid Fe/Cr alloy substrates (Crofer 22 APU, Thyssen Krupp, VDM GmbH, Germany) is shown in Fig. 2. This substrate material is designed for fuel cell applications and has a coefficient of thermal expansion that matches the SDC material. The intimate inter-lamellar contact and relatively low porosity of approximately 1.5 % in the coatings was attained at spray cond. 2 (see Table 1). A particle velocity of 691 m/sec and temperature of 3015°C was measured for zirconia at identical spray and feed conditions. Such high velocities are rarely attained in atmospheric plasma spraying. The small particles intimately follow the gas velocity as they are entrained in the plasma stream. Previous work has shown that a faster jet can dramatically increase the particle impact velocity, which, in conjunction with high particle temperatures, leads to improved flattening of the splats and densification of the coating [7]. However, the particle speed and temperature are rapidly lost at increasing spray distance. Hence, a short spray distance (~50 mm) was found to be imperative. The temperature was controlled independently by varying the suspension feed rate, thereby adjusting the total thermal load on the plasma [8]. A low feed rate of 20.2 ml/min was chosen accordingly.

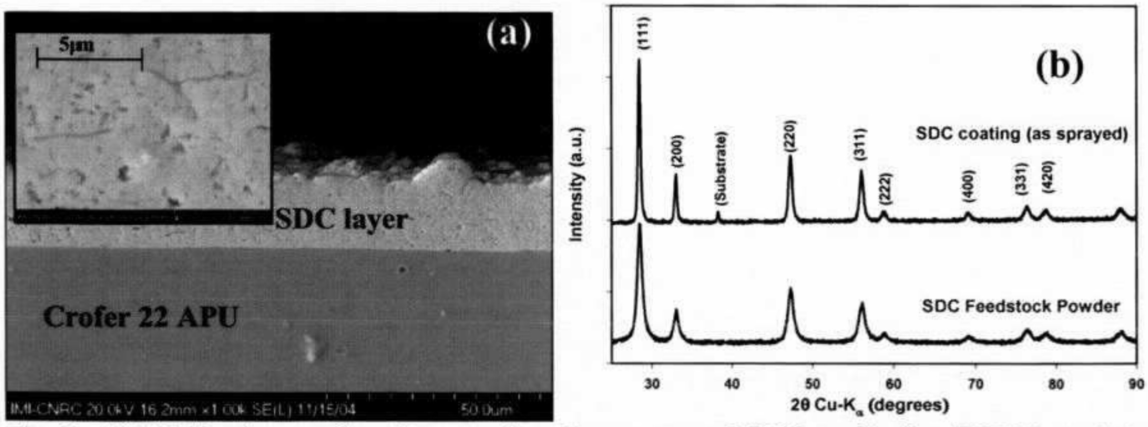

Fig. 2 : (a) SEM micrographs of suspension plasma sprayed SDC on Crofer APU 22 steel; Insert at 10,000 orig. mag.; (b) XRD spectra of SDC before and after spraying, showing CeO_2 phase.

The substrate temperature during deposition was maintained at approximately 500°C, using a specially designed substrate holder. At the short spray distance and proximity to the plasma flame, a careful thermal management, which reduces the tensile stresses created by the solidifying droplets as well as the overall thermal stresses in the assembly, was found critical to prevent vertical crack formation [9]. The XRD spectra in Fig. 2 (b) for the SDC material before and after spraying show a single phase with no or little phase transformation during the spray process. The grain size in the coating was estimated to be below 40 nm.

Electrolyte onto NiO-8YSZ The microstructure of an SDC coating deposited on a NiO-8YSZ anode is shown in Fig. 3. The anode substrates were tape casted at the NRC Institute for Fuel Cell Innovation (NRC-IFCI, Vancouver) from a 50/50 wt % mixture of NiO powder (D50:1μm, surface area 4.0 m^2/g) (Novamet, Wyckoff, NJ, USA) and 8YS (YSZ) powder (D50: 0.520μm, surface area 6.2m2/g) (Tosoh, Grove City, OH, USA). The cermet was sintered at 1250°C after casting to yield 0.6 mm thick substrates with a diameter of 16 mm and a porosity of 20.0% [10]. Continuous SDC electrolyte coatings were sprayed at cond. 2, previously optimized on the steel substrates. In spite of a careful thermal management eliminating rapid temperature changes, and using a substrate holder design, which minimizes all mechanical stresses, the freestanding cermet disks proved to be too fragile to withstand the heat flux from the plasma at the short standoff distance. The fracture cracks dissected the entire cross-section of the substrate. A stronger intimate support for these substrates was sought. Tape casting directly onto a metal support is hampered, however, by the high temperature sintering step required.

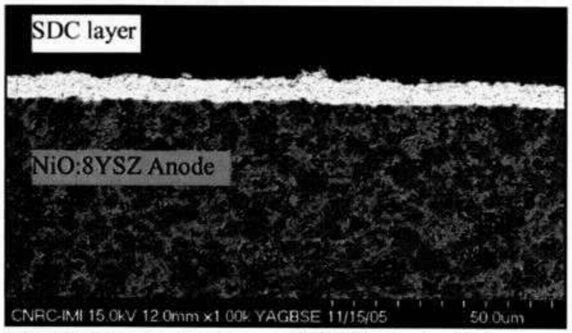

Fig. 3: Microstructure of SDC electrolyte on tape-casted NiO:8YSZ anode.

Plasma Sprayed Anode Layer. The microstructure of NiO:YSZ anode layers deposited by conventional plasma spraying directly on a metallic support is shown in Fig. 4. A porous Inconel 600 nickel alloy substrate (Applied Porous, Tariffville, CT, USA), tape-casted and sintered (2μm nominal porosity), was chosen for its resistance to oxidation and its low thermal expansion coefficient (13.3 μm/m·K). In an attempt to simulate the microstructure and porosity of the tape-casted anodes, with sufficient gas permeation in the final cell, spray conditions were selected not to fully melt all particles, but rather to allow the incorporation of partially molten particles in the coating. The fine porosity of the original feedstock is thereby partially retained.

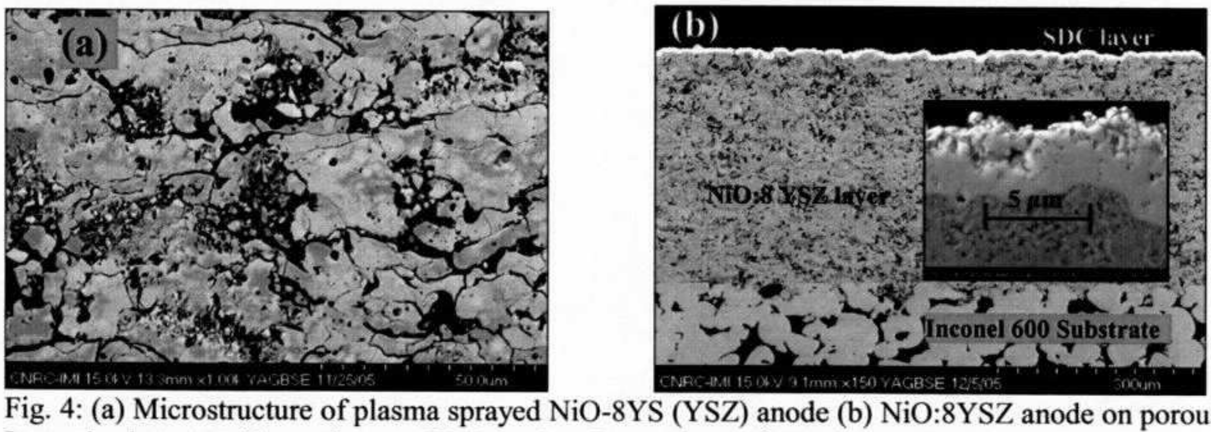

Fig. 4: (a) Microstructure of plasma sprayed NiO-8YS (YSZ) anode (b) NiO:8YSZ anode on porous Inconel substrate with continuous SDC overlay; Insert shows electrolyte and anode interface.

Process parameters, such as flow rate and composition of the process gases (Ar, H_2 and He), standoff distance and torch current were varied. At optimized conditions, an average particle temperature of 1720 ±163°C and a velocity of 229 ± 33 m/sec were measured with the DPV 2000. Even though the temperature is below the melting points of the constituents (ZrO_2 2715°C and NiO 1984°C) 30% DE was reached. An overall porosity of 18.1 ± 2.3 % (at 1000X) was attained. Besides the non-melted agglomerates, interlamellar gaps, resulting from reduced splat contact, also contributed to this porosity. The produced anode layers retained their integrity during the subsequent electrolyte deposition step by SPS. Dense SDC overlays with thickness below 10 µm were created (Fig. 5 b) The interlamellar gaps on the top surface of the anode acted, however, as points of stress release and induced occasional vertical cracks in the electrolyte at these locations. Such defects are considered detrimental, since they allow reactant gases to pass though the layer during operation of the cell.

Suspension Plasma Sprayed Anode Layers. The microstructure of SPS NiO-SDC deposits using the fine nano-powder suspension (NG) are shown in Fig. 5 (a). The coatings were produced on a solid steel substrates at spray cond. 1. A particle velocity of 550 m/sec and temperature of 2860°C was measured for ZrO_2 at those conditions. The substrate temperature was kept at 300°C.

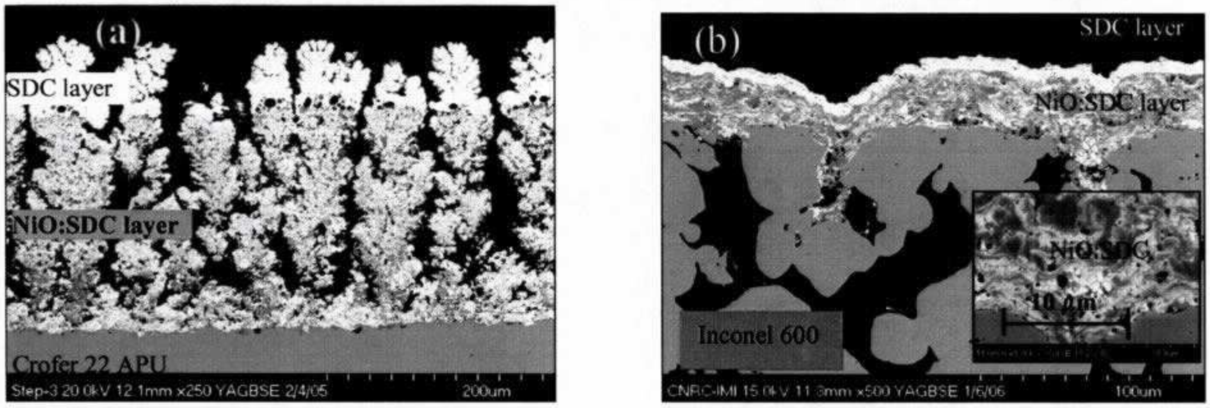

Fig. 5: (a) SPS NiO-SDC anode from fine NG feedstock, with overlaying SDC (b) SPS NiO-SDC from larger particle NT feedstock mixture, with overlaying SDC electrolyte.

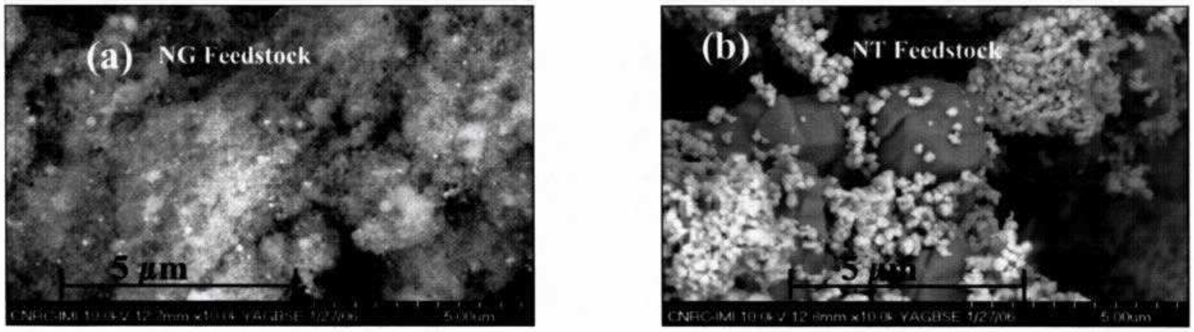

Fig. 6: SEM of (a) NiO-SDC nano-powder (NG); (b) NiO-SDC powder mixture (NT).

For diverse spray parameters investigated, an arborescence/columnar microstructure was observed. The very high open porosity and surface area of such structure may prove beneficial for SOFC electrodes in providing a high rate of gas transport and catalytic activity. It is, however, unsuitable for a processing route that requires subsequent electrolyte deposition. Dense SDC material formed locally, but a continuous SDC film could not be obtained. The creation of this unique arborescence is possibly related to the consolidation of the original feedstock into submicron particles in the suspension spray process. The loosely agglomerated nano-particles in the feedstock, as shown in Fig. 6 (a), may foster dispersion of the fine constituents instead of agglomeration into larger particles. Earlier work has shown that submicon particles intimately follow the radially deflecting gas flow in the stagnation point above the substrate [7]. Instead of impacting with a high normal velocity, those particles travel laterally along the substrate surface and possibly attach on asperities comprised in the surface roughness. The growing columns further shadow the underlying openings from the arriving particles, preventing the formation of a continuous film.

Using the significantly larger NiO-SDC feedstock powder (NT) (Fig. 6 (b)), continuous anodes were produced on porous Inconel 600 substrates (Fig. 5 (b)). At spray cond. 3, which yields particle velocities of 860 m/sec, the large pores in the metal substrate were bridged by the coating. Since the sprayed particles have at least the diameter of the original feedstock, fewer submicron particles are present in the spray process. The overall larger particles are less deflected by the turning gas in front of the substrate and impact with a higher normal velocity component [7]. The resulting splats do not foster the growth of surface discontinuities. In an attempt to provide sufficient porosity, feed rates and standoff distances were adjusted to relatively low particle temperatures (2300°C for ZrO_2). The subsequently deposited electrolyte formed a continuous film 8-10 μm in thickness, and intimately followed the surface contours of the anode. Furthermore, no vertical cracks could be detected. The absence of surface cracks may be attributable to the similarity of the anode and electrolyte in fine-scale microstructure, thermal expansion coefficient, and thermal history during creation.

Summary

Cost-effective suspension plasma spraying was implemented for the production of intermediate-temperature SOFC components. In particular, the challenge of creating thin, dense and nanostructured SDC electrolyte layers was confronted. A high heat flux from the plasma and short standoff distances were generally required to create the densest coatings. However, the proximity to the plasma flame limits the choice of substrate materials and processing route. Various routes for SOFC half-cell assemblies, using tape-cased, plasma-sprayed NiO:YSZ and suspension-sprayed NiO:SDC anodes on porous metallic interconnects, were explored. Both the plasma operating conditions, as defined by the in-flight particle velocity and temperature, as well as the feedstock particle size control the microstructure of the anode layers and their compatibility with the subsequent SDC deposition step. Of the various processing routes investigated here, the use of suspension plasma spraying for both the electrolyte and anode on a suitable metallic substrate is the most promising approach. Anodes, produced from a larger particle feedstock, permitted subsequent deposition of continuous and crack-free electrolyte layers. Ongoing work focuses on the optimization of the anode porosity and evaluation of the electrochemical performance of the IT-SOFC half-cells.

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SOFC components, such as porous NiO-SDC (nickel oxide -samarium doped ceria) anode sublayers and dense, nanostructured SDC electrolytes were fabricated. The layers were deposited by suspension plasma spraying using an axial feed dc plasma torch. The liquid carrier employed in this approach allows for controlled injection of much finer particles than in conventional thermal spraying, leading to thin coatings with refined microstructure. The superior ionic conductivity of ceria-based ceramics over conventional SOFC materials has generated considerable interest in developing cost-effective techniques for producing those coatings.

Prior to spraying an assembled system, the coatings were produced individually for varying torch operating conditions and suspension feed rates. The resulting microstructures and phase compositions were analyzed by SEM and XRD. Careful substrate temperature management during and after the spray process, in conjunction with high in-flight particle temperatures and velocities allowed for the production of dense, non-fractured electrolyte layers with thicknesses below 10μm. High porosities in the anode layers, which are required for effective gas permeation in the final cell, are attained. However, a porous microstructure of a substrate or sublayer generally implies a non-continuous and rough surface, which constitutes a principal difficulty in the subsequent electrolyte deposition. The role of suspension feedstock properties on the structure of the substrate/coating interface is discussed. Selected electrochemical properties of the coatings are shown.

Oral presentation: yes Poster presentation: no