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Evaluation of Phase Segregation in Ternary Pt-Rh-SnO_2 Catalysts Prepared from the Vapor Phase

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Ethanol holds promise as a non-toxic, transportable, energy dense (8kWh/kg) fuel that, unlike hydrogen, is amenable to use in the existing fuel infrastructure. However, slow oxidation kinetics and incomplete CO_2 formation, indicating unbroken C-C bonds at practical potentials, limit usage in a fuel cell. Incomplete formation of CO_2, a complete 12 electron transfer, leads to the formation of adsorbed intermediates such as CO, acetaldehyde, and acetic acid. These intermediates can poison the catalyst surface leading to a loss in cell efficiency. The use of Pt/Rh/Sn ternary catalysts has proven promising owing to bi-functional, electronic, and synergistic effects between the constituents. The role of Rh is to cleave the C-C bond of ethanol, SnO_2 provides the OH species to oxidize intermediates (freeing the Pt and Rd sites), and Pt is for ethanol dehydrogenative adsorption [1].

Typical synthesis methods include polyol [2], Bönneman [3], co-impregnation-reduction [4], or cation-adsorption-reduction-galvanic displacement [5] techniques. These methods however are inherently batch processes. A continuous flame-based process would allow for synthesis under highly non-equilibrium conditions through a non-aqueous route. Previous flame-based deposition of catalysts for ethanol oxidation have focused on Pt-Sn combinations and found that 10 wt.% Sn showed the best onset potential (~0.3V vs RHE) and largest oxidation peaks in 0.5 M H_2SO_4 and 1 M ethanol at 1 mV/s [6]. Reactive spray deposition technology (RSDT) has been developed by Maric et al. to produce nanoparticles in vapor phase for catalysts comprised of Pt [7,8], $Ir_xPt_{1-x}O_{2-y}$, and $Ir_xRu_{1-x}O_{2-y}$ [9]. In this work we extend recent studies on Pd-Ru and Pd cores made by the RSDT process, with subsequent Pt monolayer attachment by galvanic displacement, to the ternary Pt/Rh/Sn system. Elemental ratios of 3:1:3 and 3:2:3 are examined for their performance toward ethanol oxidation.

Microscopy studies are presented to better understand the unique morphology and elemental distribution that results when nanoparticles are formed by nucleation from the gas phase. Figure 1A shows the nodular morphology of Pt/Rh/Sn (3:2:3) as grown (direct deposit) on a gas diffusion layer while Figs. 1B-G show the XEDS elemental mapping of Sn, C, O, Pt, and Rh. Figures 2A-B are STEM images of the electrode after electrochemical testing. Figs. 2C-F the XEDS mapping from a Titan G2 80-200. The XEDS was mapped using the windowless silicon drift detector Super-X system.

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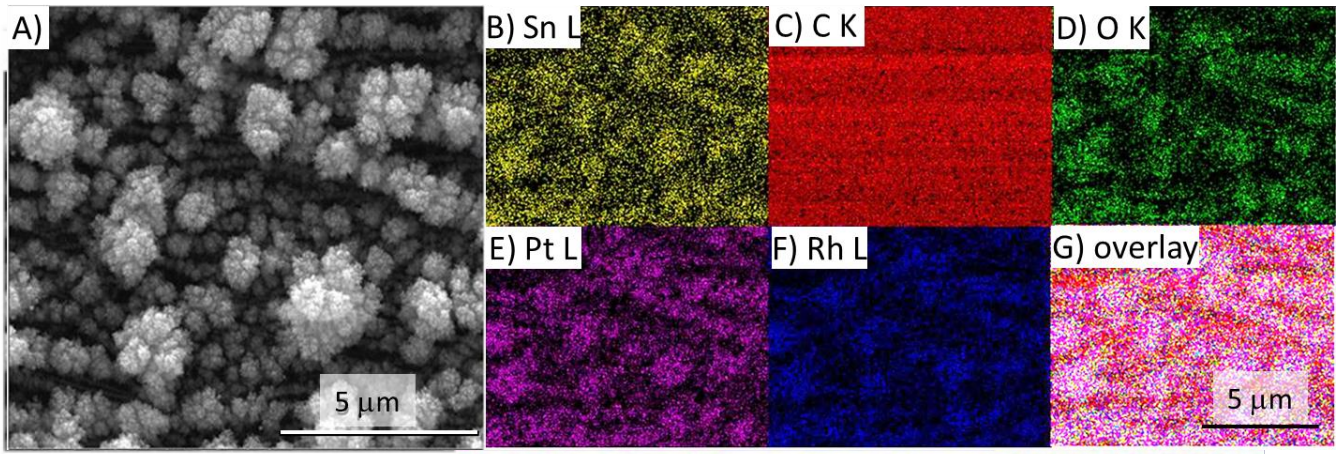

Figure 1. a) Morphology of Pt/Rh/Sn (3:2:3) as deposited onto a Sigracet SGL 25-BC gas diffusion layer and B-G) the XEDS elemental distributions.

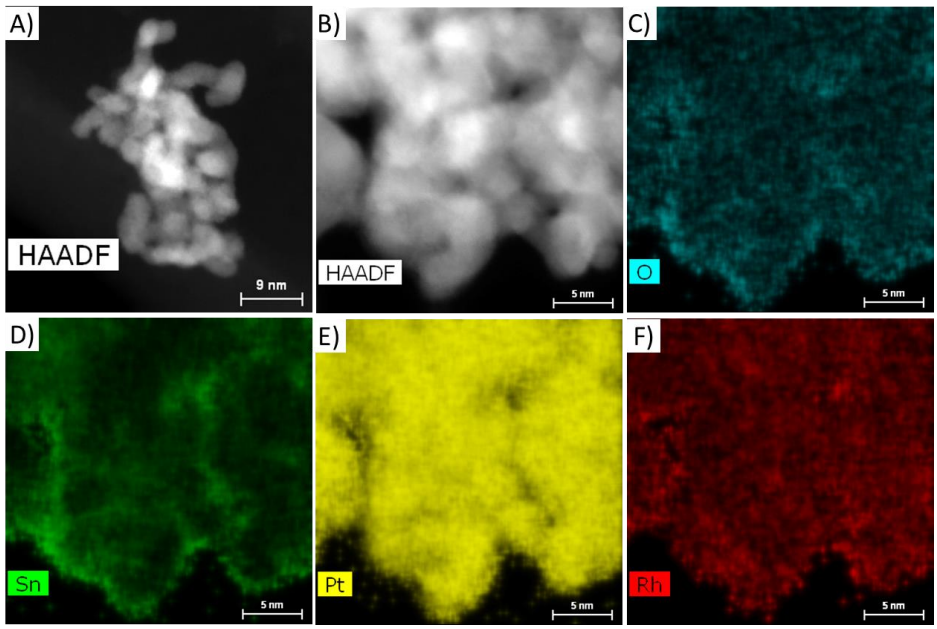

Figure 2. STEM image with XEDS mapping of an electrode section that was previously tested toward ethanol oxidation. A) Shows a piece of the electrode comprising many individual nanoparticles while B-F) show another area with the corresponding elemental mapping.

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