

Hydrogen evolution on combustion catalyzed electrodes with low loadings for PEM Electrolyzers

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Proton exchange membrane water electrolysis (PEMWE) is industrially important as a green source of high purity hydrogen both in chemical feedstock applications as well as in energy storage. The rapid response time of electrolyzers to power fluctuations; a compact footprint; reliability; cycle life; and no CO₂ generation, when powered by renewable energy sources, make this technology ideal to capture generated electrical capacity that would otherwise be curtailed. Water based electrolyzers with lower heating value voltage efficiencies of 75% are projected to be able to produce H₂ in the \$3-4/kg range assuming reasonable electricity costs of \$0.05/kW-hr [1].

Current PEM electrolyzer cost drivers are low volume manufacturing and high stack component costs; the current commercial units use >2 mg/cm² of precious group metals (PGM) in both the anode (oxygen evolution reaction, OER) and cathode (hydrogen evolution reaction, HER). The O₂ evolution at the anode suffers from large overpotential losses and durability issues that affect the efficiency and stability of this electrode. This electrode must endure high potentials (>2 V) and an acidic environment. Under these conditions carbon is easily oxidized and above 1.5V even un-alloyed noble metals such as Pt and Pd are corroded. Due to the high cost of the PGMs, which dominate electrolysis catalysis, a strategy of reduction through increased utilization and alloying is required. Extended surface area catalysts (*i.e.*, 3M's NSTF platform) of PtIrRu and PtCoMn have been recently evaluated as a strategy to that employs both structure and alloying to reduce cost [2].

The Reactive Spray Deposition Technology (RSDT) approach is an ideal candidate for eliminating substantial direct MEA fabrication costs as well as indirect energy costs [3-6]. The RSDT route eliminates several process steps required in ink baseline processes and effectively combines catalyst synthesis, film formation, and support mixing into one step as shown in Figure 1.

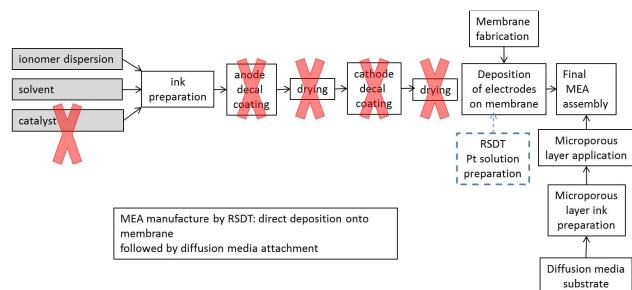


Figure 1: Elimination of MEA decal transfer and ink preparation steps by the RSDT process

In the RSDT process, a film is grown from the dry state directly onto a substrate in the open atmosphere using a

combustion nozzle. The solute (*e.g.*, xylene) has a dual role by acting both as a cheap solvent, and as a fuel; xylene releases its enthalpic heat of combustion to decompose the metal cations and hydrocarbon anions. The xylene is atomized and subsequently oxidized (*i.e.*, combusted) into CO₂ and H₂O. The precursor, once the droplet exits the nozzle, proceeds through the following stages: heats up to the boiling point of the solvent; precipitates due to a rapid solvent shell volume decrease (*i.e.*, simultaneous evaporation and combustion); decomposes; phase changes from solid to vapor; and finally undergoes a series of redox reactions. M⁺ is reduced to M (M=metal) or oxidized depending on the relative Gibbs free energy of formation and stability of the oxide as a function of pO_2 and temperature (*e.g.*, location on an Ellingham diagram).

Formation of the nanocrystallite particles, during time-of-flight, occurs prior to film formation through a multi-step process on a time scale of milliseconds. The general mechanism of particle growth, once the precursor has vaporized, occurs by: homogeneous reactions, nucleation, surface growth, cluster dynamics (a transitory state between single atoms and solid material), coalescence, aggregation, and agglomeration [7]. Ballistic nanoparticle impingement is the mechanism of film formation; although a mechanism involving some fraction of film growth directly from the vapor phase cannot be ruled out.

Recent proof-of-concept work has shown the feasibility of using RSDT to directly deposit Ir_xRu_{1-x}O_{2-y} and Ir_xPt_{1-x}O₂ OER films [8-9]. The applicability of directly forming HER and OER electrodes by RSDT into gas diffusion electrodes (GDEs) and catalyst coated membranes (CCMs) for PEMWEs is discussed as an extension of this work. RDE experiments using Pt HER electrodes are performed. Benchmarking of an RSDT applied HER cathode against Proton OnSite's existing commercial catalyst is discussed using a 25cm² platform at 50 and 80°C. Alternate supports to carbon are necessary to increase metal dispersion and a wide range of possibilities are currently being explored for PEMFCs [10]. In light of these non-carbon support options, a Pt dispersion onto a doped Ti_nO_{2n-1} is evaluated for the HER reaction.

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