



Flame-based processing as a practical approach for manufacturing hydrogen evolution electrodes



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HIGHLIGHTS

- A deposition study is employed using RSDT to deposit catalysts in onestep.
- All combinations of catalyst with Nafion[®] as the binder remained intact after polarization.
- Processing conditions can result in either amorphous or crystalline Pt.
- Deposition of Pt/Vulcan XC-72R onto Toray paper resulted in the best performance.
- The RSDT GDE configuration operated at 70% efficiency with a 5× reduction in Pt.

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ABSTRACT

Catalyst structure and morphology are inevitably dictated by the synthesis route, which in-turn dictates catalyst activity, stability and utilization in the electrode. Reactive spray deposition technology (RSDT) is a promising synthesis route for electrode manufacturing because of the potential to achieve high-throughput processing under a diverse range of process configurations. This work investigates several unique approaches to Pt catalyst deposition using jet-flame synthesis for water electrolysis electrodes. Direct application of the catalyst film onto Nafion 117 and carbon paper is explored along with approaches to dispersing the Pt onto carbon or Ti_nO_{2n-1}. Operational challenges relating to the harsh conditions of H₂ evolution and electrode adhesion are addressed by adding binder and catalyst support to the electrode structure. The RSDT technology produces an electrode, coated directly onto Nafion 117[®], with a 20-fold reduction in Pt loading while maintaining high in-cell performance (2.1 V at 2 A cm⁻²) compared to an industry-level baseline. Durability testing at 1.8 A cm⁻², 400 psi differential pressure and a temperature of 50 °C yields a consistent potential of ~2.2 V for over 1100 h without failure. The same electrode applied directly to carbon paper resulted in a voltage of ~2.1 V for ~600 h without failure.

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1. Introduction

1.1. Hydrogen

Hydrogen is a widely used industrial gas, with a large and expanding global market. Over 10 million metric tons of hydrogen are produced in the US each year [1]. High-purity hydrogen is used in a variety of applications including fuel cell operation, electric generator cooling, chemical production, heat treating, semiconductor processing, and as a laboratory carrier or fuel gas. Hydrogen also has the potential to become a significant alternative

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fuel because it offers a range of potential benefits including increased energy security, reduced dependence on foreign oil, and reduced greenhouse gas emissions. As a potential energy storage carrier, hydrogen can serve as a link between electric and gas infrastructures and provide ancillary services to the grid such as frequency regulation and load shifting.

1.2. Membrane-based electrolysis

Proton exchange membrane (PEM)-based systems have many advantages over other hydrogen production technologies. Compared to hydrocarbon steam reforming, PEM technology is more environmentally friendly, especially when combined with a renewable energy source, and easily scales down, enabling efficient, cost-effective on-site production and reduces the need to ship hydrogen from a centralized location. In addition, membrane-based electrolysis produces very pure hydrogen, with none of the typical catalyst poisons that are found in hydrogen produced from reforming. PEM-based systems do not require corrosive electrolytes such as those used in the liquid potassium hydroxide (KOH) electrolyte-based systems. In addition, PEM-based systems have a more compact footprint, and the ability to generate hydrogen at high pressure while operating at ambient oxygen pressure, which increases safety and reduces cost compared to KOH-based systems.

For energy storage applications, PEM electrolysis has been selected as the technology of choice [2]. The cell stacks respond quickly and robustly to variable input load, thus enabling a variety of energy capture applications. Siemens has recently announced that their product development will focus on PEM electrolysis, and even companies with established KOH-based products are investigating PEM technology for energy applications [4]. While PEM-based systems have many advantages, significant development in materials and manufacturing are needed for large-scale energy applications.

For example, most commercial electrolyzers use unsupported catalysts and manual electrode fabrication and testing processes. This results in high noble metal loadings and high labor costs to manufacture the membrane electrode assembly (MEA), which accounts for nearly one-fifth of the total stack cost. As the development of larger scale electrolysis for energy applications becomes closer to reality, higher MEA manufacturing speed, lower manufacturing energy, and lower catalyst loadings are essential for market success.

1.3. Ultra-low loading

Conventional electrode fabrication processes involve multiple manual steps such as mixing of catalyst and binder materials, inking, sintering, and decal transfer in a high temperature press. Reduction in the thickness of the electrode layer (and consequently reduction in catalyst loading), while still achieving acceptable uniformity, is challenging in the current process.

Electrolysis electrodes have to withstand different operating conditions than fuel cell electrodes, such as significantly higher potential on the oxygen electrode, full humidification with high water uptake, and high mechanical stress due to gas evolution at high current densities, resulting in large amounts of bubble formation at the electrode surface. Alternate fabrication processes that provide tunable control over electrode structure, such as spraying [5,6], sputtering [7], nano-structured thin-films [8], and flame spray pyrolysis [9–11] are, therefore, key areas for development.

1.4. RSDT

RSDT is a variant of flame spray pyrolysis (FSP) [12] and spray pyrolysis (SP) [13]. The RSDT approach uses the combustion

enthalpy of a solvent to decompose the precursor in the turbulent confines of a jet-flame. Catalyst production and electrode formation are combined into one step, which takes place in the open atmosphere and eliminates the need to dispose of solvent waste; the solvent is completely combusted to CO_2 and H_2O . A wide array of material systems have been made using RSDT including Pt, CeO_2 , SnO_2 , Sn–Pt, LiCoO_2 , $\text{Ir}_x\text{Pt}_{1-x}\text{O}_{2-y}$, $\text{Ir}_x\text{Ru}_{1-x}\text{O}_{2-y}$ and $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ [10,11,14–21].

Nucleation of the metal occurs from the vapor phase, along with growth of the primary particle throughout the length of the hot reactive zone [22] as shown in Fig. 1. 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 formation (a transitory state between single atoms and solid material), coalescence, aggregation, and agglomeration [23–26]. Depending on the processing conditions, a film can form either from the vapor phase (*i.e.*, direct impingement of the flame onto the substrate), by a physical impingement (ballistic deposition) of a fully formed nanoparticle, or by a combination of both mechanisms. The exact growth mechanism is affected by the synthesis thermal profile, concentration of reactants, the precursor composition, oxidant/fuel flow rates, and residence time. In co-flow atomizing-burners, the oxidant and fuel flow rates, combined with the exit orifice geometries, strongly affect the mixing [27–29]. The mixing determines residence time and temperature profile of the flame.

Primary particle growth can be arrested through rapid cooling by an air quench (labeled ‘quench point’ and denoted as a vertical line in Fig. 1), to create a fast non-equilibrium phase change [30]. Stand-off distance, temperature and location(s) of the quench are also critical to the formation of the desired metal and morphology [25]. The quench has two distinct functions: it stops particle growth, and it allows a wider range of substrate materials to be positioned at lower stand-off distances. This is crucial for direct deposition onto polymeric electrolytes such as Nafion[®] which has a glass transition point at 110 °C [31]. While passing through the quench, the temperature drops 200–400 °C cm^{-1} and the luminosity of the flame is greatly diminished. The post-quench product stream consists of nanoparticles that can enter into an optional secondary spray zone where two air-assist atomizers inject a suspended support material into the cooled reactant gas stream. The droplets are entrained and mixed with the process stream prior to striking the substrate.

In this work, RSDT was used to prepare new high performance electrode structures for hydrogen evolution in PEM-based water electrolysis. Specifically, this study investigated the deposition of hydrogen evolution catalysts under varying quench temperatures and flow rates. The prepared electrodes were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrode and cell configuration adjustments, and variable cell testing conditions were used to understand the most important parameters and guide development.

2. Experimental

2.1. Chemicals and materials

Pt acetylacetonate ($\text{Pt}(\text{acac})_2$, Colonial Metals, Elkton, MD) was used as the Pt source. $\text{Pt}(\text{acac})_2$ is one of the most highly available and least expensive organoplatinum compounds, and is widely used in catalysis [32,33]. Additionally it is free of potential halide or

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