

Pt nano-particle performance for PEFC reactions at low catalyst loading and high reactant mass transport

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Background

Understanding the electrocatalytic performance of the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) on Pt nano-particles is vital for polymer electrolyte fuel cell (PEFC) development.

The majority of fundamental research on the two reactions is performed with a rotating disk electrode (RDE). While the RDE is a powerful technique, being submerged in electrolyte limits the overpotential range that can be studied before mass transport effects become dominant. At the rotation rate limit of $\sim 10\text{K rpm}$, the limiting mass transport current densities are only 14 and $6 \text{ mA cm}^{-2}_{\text{Geo}}$ for the ORR and HOR, respectively.¹ PEFCs operating with pure hydrogen and oxygen can have current densities up to three orders of magnitude higher than this. Therefore, data from the RDE is generally extrapolated to PEFC current densities, which can introduce significant errors.

Measuring the catalytic activity within a PEFC would be the most desirable method. However, these studies are limited by the fuel cell design and operation, proving intricate and time consuming to optimize for fundamental studies²

- It is challenging to minimize concentration gradients of reactants, products and water distribution across a flow field of a PEFC, generally from the inlet to the outlet and also under channel and land.
- A two electrode configuration is typically used, causing the measured signal to be a contribution of both electrodes. A reliable three electrode setup, although highly desirable for kinetic studies, is difficult to realize in an operating PEFC.
- Hydrogen crossover results in a parasitic current on the order of $\text{mA cm}^{-2}_{\text{Geo}}$ that has to be corrected for on analysis.

Abstract

An alternative approach to measure the electrocatalytic performance of fuel cell reactions is presented.³ The approach combines high mass transport with a flat, uniform, and homogeneous catalyst deposition

process, well suited for studying intrinsic catalyst properties at realistic operating conditions of a PEFC.

Uniform catalyst layers utilising standard fuel cell catalysts were deposited onto a porous substrate to loadings as low as $0.16 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ and catalyst layer thicknesses as low as 200 nm . Such ultra thin catalyst layers are considered advantageous to minimize internal resistances and mass transport limitations. The electrodes were floated on aqueous electrolyte, whereby reactant gas diffused through hydrophobized pores to the catalyst layer. Modelling of the associated diffusion field suggests that such high performance is enabled by fast lateral diffusion within the catalyst layer. The electrodes operate over a wide potential range with insignificant mass transport losses, allowing the study of the ORR kinetics at high overpotentials, Figure 1.

Geometric current densities as high as $5.7 \text{ A cm}^{-2}_{\text{Geo}}$ were experimentally achieved at a loading of $10.15 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ for the HOR at room temperature, which is three orders of magnitude higher than current densities achievable with the RDE. Electrodes produced a specific current density of $31 \pm 9 \text{ mA cm}^{-2}_{\text{Spec}}$ at a potential of 0.65 V vs. RHE for the ORR and $600 \pm 60 \text{ mA cm}^{-2}_{\text{Spec}}$ for the peak potential of the HOR.

The mass activity of a commercial 60 wt\% Pt/C catalyst towards the ORR was found to exceed a range of literature PEFC mass activities across the entire potential range. The HOR revealed fine structure in the limiting current range and an asymptotic current decay for potentials above 0.36 V . These characteristics are not visible with techniques limited by mass transport in aqueous media such as the RDE.

This technique lends itself to high throughput testing of novel catalysts and fundamental analysis where high mass transport is needed; such as analysis of particle size effect for the HOR, previously challenging to measure.

References

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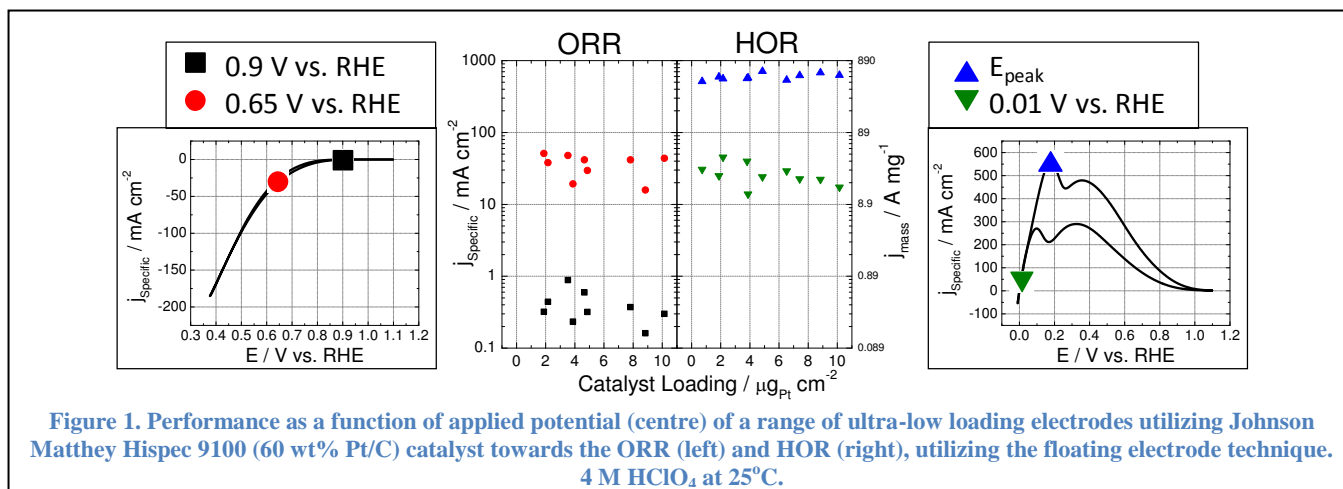


Figure 1. Performance as a function of applied potential (centre) of a range of ultra-low loading electrodes utilizing Johnson Matthey Hispec 9100 (60 wt% Pt/C) catalyst towards the ORR (left) and HOR (right), utilizing the floating electrode technique. 4 M HClO_4 at 25°C .