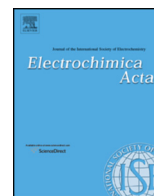




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Benchmarking Pt-based electrocatalysts for low temperature fuel cell reactions with the rotating disk electrode: oxygen reduction and hydrogen oxidation in the presence of CO (review article)

Christoffer M. Pedersen^{a,b}, María Escudero-Escribano^b, Amado Velázquez-Palenzuela^b,
Leif H. Christensen^a, Ib Chorkendorff^b, Ifan E.L. Stephens^{b,*}

^a Center for Nano- and Micro technology, Danish Technological Institute (DTI), Gregersensevej, DK-2630 Taastrup, Denmark

^b Center for Individual Nanoparticle Functionality, Department of Physics, Building 312, Technical University of Denmark (DTU), DK-2800 Lyngby, Denmark

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ABSTRACT

We present up-to-date benchmarking methods for testing electrocatalysts for polymer exchange membrane fuel cells (PEMFC), using the rotating disk electrode (RDE) method. We focus on the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR) in the presence of CO. We have chosen our experimental methods to provide the most optimal compromise between the ease of carrying out the measurements and for ensuring comparability with PEMFC conditions. For the ORR, the effect of temperature, scan rate, Ohmic drop correction and background subtraction on the catalyst activity is investigated, both on a polycrystalline Pt disk and two different commercial Pt/C catalysts. To benchmark the CO tolerance of HOR catalysts, cyclic voltammetry and chronoamperometry are used, on polycrystalline Pt and commercial catalysts consisting of Pt/C and PtRu/C. We recommend the optimal conditions for obtaining a benchmark of ORR activity and CO tolerance of HOR catalysts.

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1. Introduction

Low-temperature fuel cells, in particular Proton Exchange Membrane Fuel Cells (PEMFCs) could take a pivotal role in a future society based on sustainable energy. They convert chemical energy efficiently into electricity; should the hydrogen be derived from splitting water, they would emit negligible CO₂ emissions. PEMFCs can be used complementary to batteries for powering zero CO₂ emission vehicles. One of the chief advantages of using PEMFCs in automobile applications, over batteries, is the high energy density. For long range vehicles (~500 km range) the PEMFC energy storage system can be made about six times lighter than for a similar advanced Li-ion battery system [1,2]. Analysis of zero emission vehicles suggest that fuel cell vehicles are more economically viable for the longer range vehicles whereas for urban transport (~160 km range) batteries are the better choice [1–3]. Another practical advantage is that it is much faster to refuel hydrogen than it to recharge a similar sized battery. However, the high cost of PEMFCs, together with their relative limited lifetime compared to competing technologies is hindering wide adaption of this

technology [4]. Part of the high cost is due to the high Pt loading necessary at the cathode (0.4 mg_{Pt}/cm²), where the oxygen reduction reaction (ORR) takes place [4–7]. To reduce costs, the Pt loading should be reduced by increasing the activity of the ORR catalyst. Tremendous progress has been made in improving the activity for the ORR in the last decade [8–31].

Scalable Pt-alloy catalysts are now implemented in PEMFC's with activity and stability that exceed performance targets set by the DOE for 2020, listed in Table 1 [31]. However, even when the DOE targets are obtained, it would still only be possible to produce 17.4 million fuel cell vehicles a year (assuming 12.5 g per 100 kW, and using worldwide production of platinum in 2012: 218,000 kg [33]). In comparison, ~87.4 million vehicles were produced worldwide in 2013 [34]. Moreover, although state-of-the-art alloys often perform well in accelerated degradation tests [27,28,31], it is not clear how well they will perform over the long term in PEMFCs [35].

It is worth bearing in mind that should the Pt-loading in PEMFC's be decreased by an order of magnitude, they will reach a similar level to the amount currently used in advanced catalytic converters [3,6]. This means that a catalyst is required with a stable activity of around 1.6 A/mg mass activity at 0.9 V, when measured in a fuel cell. Fig. 1 shows the specific activity (a) and mass activity (b) of a selection of some of the most active ORR catalysts. We have

* Corresponding author.

E-mail address: ifan@fysik.dtu.dk (I.E.L. Stephens).

Table 1
–Summary of DOE targets for catalyst in automotive applications from the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [32].

	2020 Target
Pt group metal total content (both electrodes)	0.125 g kW ⁻¹
Pt group metal total loading	0.125 mg cm ⁻²
Loss in initial catalytic activity (mass activity)	<40%
Catalyst support stability (mass activity loss)	<10%
Mass activity @ 0.9 V vs RHE	0.44 A mg _{Pt} ⁻¹

normalised the mass activity to the total mass of precious metal, as opposed to the total mass of Pt only (for example a metal like Au has a similar cost to Pt, and a metal like Pd may currently be cheaper, but has similar supply limitations to Pt). The comparison of these different data is sometimes challenging, especially as different experimental conditions have been applied, including (a) temperature (b) scan rate (c) correction of Ohmic losses (d) subtraction of background capacitive currents. Several articles have addressed some of these parameters, in order to develop more meaningful benchmarks [5,36–40]. However, given that this is a rather fast moving field, we take the view that there is a need for an updated overview of how these different parameters affect the measured catalyst activity.

The anode of low-temperature PEMFCs, where the oxidation of hydrogen takes place, can operate with much lower Pt loadings than the cathode (where the ORR occurs), when pure H₂ is used. Loadings as low as 0.05 mg/cm² can be used in a fuel cell and still drive currents on the order of A/cm² at negligible over potential [4,41]. Indeed, on Pt/C, due to the ultra-fast kinetics of hydrogen oxidation, in combination with the low solubility of H₂ in liquid

electrolytes, rotating disk electrode (RDE) based techniques grossly underestimate the activity of the catalyst by orders of magnitude [42–47].

The majority of H₂ produced today is derived by reforming fossil fuels. This is because the high purity grade H₂ produced from electrolysis is expensive, due to the greater energy input required to produce it. Reformate hydrogen contains trace amounts of CO; the HOR activity of Pt is significantly degraded when CO concentrations as low as 10 ppm are present in the anode feed gas [4,48,49]. In automotive applications, the varying reformate gas flows due to varying power demands, makes it difficult to achieve CO content in the <10 ppm range [4] resulting in substantial performance losses induced from CO poisoning. One strategy to mitigate the effect of CO is to air-bleed the anode [50], by feeding the reformate H₂ with ~2% O₂; this oxygen oxidises the CO to CO₂ [4]. A major disadvantage of using air-bleed is the increased production of H₂O₂ which degrades the membrane [51]. Another solution to CO poisoning is to develop CO-tolerant HOR electro catalysts for low-temperature fuel cells that could be fed with impure hydrogen produced by reforming of hydrocarbons. This has been achieved by alloying Pt with other metals such as Ru [52–54], Sn [54,55], Mo [56,57], Fe, Co and Ni [58,59]. Pt–Ru exhibits the most superior performance of these catalysts due to its higher activity at low potentials 0–0.2 V vs RHE [60]. At more positive potentials, above 0.3–0.4 V vs RHE, i.e. in the *post-ignition* region, the CO-tolerance of this catalyst is by virtue of the bifunctional electrooxidation of CO to CO₂: Ru activates water and Pt activates CO [61–63]. However, for fuel cell applications, the activity below 0.3–0.4 V vs RHE, i.e. in the *pre-ignition* region, is of much greater relevance. Under such conditions, even Pt–Ru is unable to oxidise CO; on the other hand, the Pt-surface atoms will

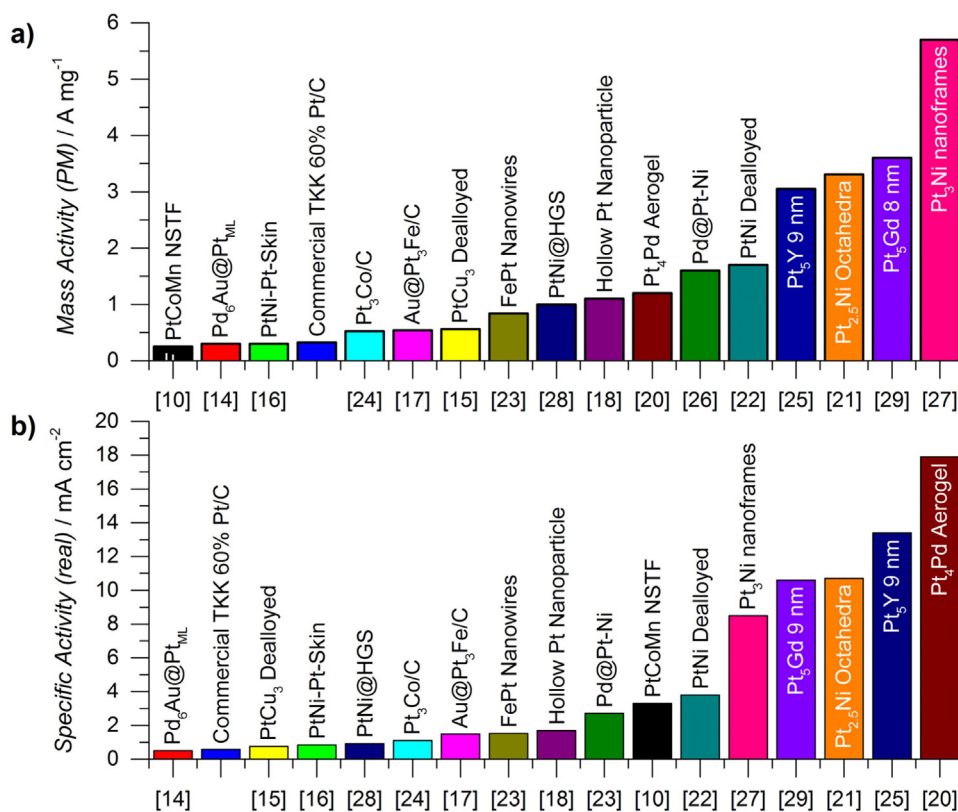


Fig. 1. Showing a) mass activity and b) specific activity at 0.9 V vs RHE for a selection of nanoparticulate catalysts reported in literature. Data adapted from [10,14–18,20–29]. In cases where either the mass activity or specific activity was specified directly at 0.9 V vs RHE it has either been found from digitized data in supporting information found in [20]; converting between mass activity and specific activity using specified electrochemical surface area [21,27]; or in the case of [14,16] using extrapolated data by Baldizzone et al. [28]. Note that the mass activity of Pd₅Au@Pt_{ML} and Au@Pt₃Fe/C have been normalized to Pt mass and not precious metal (PM) like the rest.

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