



# The importance of ultrasonic parameters in the preparation of fuel cell catalyst inks



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## ABSTRACT

We report here that ultrasound (20 kHz and 40 kHz) affects the catalyst ink composition when irradiated for longer periods and at high ultrasonic powers. In our study, two commercial carbon supported Pt (Pt/C) catalysts were used and dispersed in Nafion<sup>®</sup> ionomer. Catalyst ink samples prepared from Nafion<sup>®</sup>, IPA and water were either ultrasonicated (20 kHz up to 12.23 W and 40 kHz at 1.82 W) or mechanically shear-mixed (19,000 rpm) for various durations (up to 120 min). All catalyst ink samples were characterised by XRD, BET, TEM and electrochemical measurements were performed in liquid electrolytes. It was found that an optimised ultrasonic treatment is required to improve the catalytic ink activity, but longer irradiation is detrimental to its composition and morphology, mainly due to cavitation and sonolysis phenomena.

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## 1. Introduction

There are numerous well-documented methods describing the preparation of PEMFC and DMFC catalyst inks. For example, Litster and McLean [1] and Wee et al. [2] give excellent overviews of PEMFC catalyst ink and electrode fabrication methods. It is common for catalyst inks to be mixed ultrasonically for a few minutes or hours (typically by immersion in laboratory ultrasonic cleaning baths in the range of 38–40 kHz) in order to produce a homogeneous mixture of carbon-supported Pt catalyst and ionomer binder, which is essential in order to maximise catalyst utilisation at the ‘three-phase reaction zone’ (also known as the Triple Phase Boundary – TPB).

For the last 20 years, there have been a few reports on the use of ultrasound for fabricating noble metal nanoparticles, catalysts and other fuel cell materials. Pollet [3] showed in his comprehensive review that the ultrasonic, sonochemical and sono-electrochemical methods used for the preparation of *mono*- and *bi*-metallic nanoparticles, carbon-supported electrocatalysts (via the ultrasonic functionalisation of the carbonaceous material), fuel cell electrodes and membranes offer unique and often highly

advantageous experimental conditions by virtue of ultrasound-induced cavitation, water sonolysis and enhanced mass transport phenomena.

Ultrasound is defined as a sound wave with a frequency above 16 kHz with the upper limit usually taken to be 5 MHz for gases and 500 MHz for liquids and solids [4]. The application of ultrasound in chemical, physical and biological sciences can be divided into two main groups: (i) low frequency or power ultrasound (20–100 kHz) and (ii) high frequency or diagnostic ultrasound (2–10 MHz). Diagnostic ultrasound is often used in chemical analysis, medical scanning and in the study of relaxation phenomena [4]. Low amplitude waves are often used to determine the velocity and absorption coefficient of the sound wave by the medium, i.e. the effect of the medium on the ultrasonic wave. However, power ultrasound can be regarded as the effect of the sound wave on the medium. Low frequency and high energy waves are used in ultrasonic cleaning, drilling, soldering, chemical processes and emulsification [4].

Over the past few years the use of power ultrasound has found wide applications in the chemical and processing industries where it is used to enhance both synthetic and catalytic processes and to generate new products. This area of research has been termed *sonochemistry*, which mainly concerns reactions involving a liquid leading to an increase in reaction rates, product yields and erosion of surfaces [4]. However, the main reason for most of the observed effects of ultrasound on surfaces and chemical reactions is recognised as being due to ‘cavitation’ effect which occurs as a

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secondary effect when an ultrasonic wave passes through a liquid medium.

Cavitation was first reported in 1895 by Thorneycroft and Barnaby [5] when they observed that the propeller of a submarine eroded over short operating times, caused by collapsing bubbles induced by hydrodynamic cavitation in turn generating intense pressure and temperature gradients locally. In the late 1920s, Rayleigh [6] published the first mathematical model describing 'cavitation' in incompressible fluids. It was not until 1927 that the use of ultrasound on chemical and biological systems was first observed and recognised as a useful tool by Richard and Loomis [7].

Cavitation is a phenomenon where microbubbles are formed which tend to implode and collapse violently in the liquid leading to the formation of high velocity jets of liquid. Indeed, ultrasound consists of alternating compression and rarefaction cycles (Fig. 1). During rarefaction cycles, negative pressures developed by the high power ultrasound are strong enough to overcome the intermolecular forces binding the fluid. The succeeding compression cycles can cause the microbubbles to collapse almost instantaneously with the release of a large amount of energy. Bubble formation is a three-step process consisting of nucleation, bubble growth and collapse of gas vapour filled bubbles in a liquid phase. These bubbles transform the low energy density of a sound field into a high energy density sound field by absorbing energy from the sound waves over one or several cycles and releasing it during very short intervals. Cavitation phenomenon is known to cause erosion, emulsification, molecular degradation, sonoluminescence and sonochemical enhancements of reactivity solely attributed to the collapse of cavitation bubbles [4]. It is now well accepted in the field that the cavitation bubble collapse leads to near adiabatic heating of the vapour that is inside the bubble, creating the so-called "hot-spot" in the fluid, where:

- (1) High temperatures (ca. 5000 K) and high pressures (ca. 2000 atms) are generated with cooling rates of  $10^{9-10} \text{ K s}^{-1}$  during the collapsing of cavitation bubbles are observed. Here, water vapour is 'pyrolyzed' into hydrogen radicals ( $\text{H}^\bullet$ ) and hydroxyl radicals ( $\text{OH}^\bullet$ ), known as water sonolysis (Fig. 1).
- (2) The interfacial region between the cavitation bubbles and the bulk solution is paramount. The temperature is lower in the interior of the bubbles than the exterior but high enough for thermal decomposition of the solutes to take place with greater local hydroxyl radical concentrations in this region.
- (3) The reactions of solute molecules with hydrogen atoms and hydroxyl radicals occur in the bulk solution at ambient temperature.

Because of ultrasound's 'extraordinary' effects, extensive work has been carried out in which high power ultrasound (20 kHz to 2 MHz) was applied to various chemical processes leading to several industrial applications and many publications over a wide range of subject areas [4]. It has been shown that the effects of high intensity ultrasonic irradiation on chemical processes lead to both chemical and physical effects, for example, mass-transport enhancement, surface cleaning and radical formation via sonolysis due to cavitation phenomena (Fig. 2) [4].

Our own literature search revealed that nearly 90% of low temperature fuel cell catalyst ink preparations use ultrasound (usually ultrasonic cleaning baths) for the efficient dispersion and homogenisation of the catalyst inks prior to PEMFC and DMFC electrode fabrication. In some cases, the literature indicates that: (i) the ultrasound source type (horn or bath), ultrasonic frequency, power, intensity and irradiation time are not reported, and (ii) temperature is not often controlled, regulated and reported (it is well-known that power ultrasound yields rapid temperature rises with  $\Delta T$ s of up to  $\sim +50^\circ\text{C}$  in short

exposure times e.g. up to 1 hour in water starting from room temperature). In other cases, ultrasound time is mentioned and varies from 5 min to 24 h ultrasonication from one study to another.

Two fairly recent papers published by Takahashi and Kocha [8] and Garsany et al. [9] describe the importance of catalyst ink optimisation when evaluating electrocatalysts activities towards the ORR (Oxygen Reduction Reaction) in liquid electrolytes using the RDE (Rotating Disc Electrode) methodology. The authors highlighted the importance of producing good dispersion with the catalyst ink prior to deposition on an electrode. Good catalyst ink dispersions were qualitatively identified by ultrasonication of the catalyst ink and allowing it to rest without stirring for a period of time. Electrochemical Surface Area (ECSA) was used as the quantitative parameter in order to decide whether the catalyst ink dispersion was optimal. For their baseline Pt/C (C: Vulcan XC-72R) catalyst, their study showed an increase in the ECSA from  $80$  to  $100 \text{ m}^2 \text{ g}^{-1}$  (25%) whereas for their Heat-Treated (HT) Pt/C-HT catalyst an even more drastic variation was observed ( $35\text{--}74 \text{ m}^2 \text{ g}^{-1}$ ). They observed that the important factor in the catalyst ink optimisation was the ratio of IPA to water (found to be  $\sim 35\%$ ) in the catalyst ink formulation as well as the energy and duration of the subsequent ultrasonic treatment. It was observed that for a given catalyst ink composition, ultrasonication times of less than 5 min showed irreproducible results, and durations greater than 10–15 min were found to be sufficient for all the catalyst inks studied. Beyond 15 min and for up to a period of 3 h, the effect of continued ultrasonication was found to produce no observable degradation in terms of loss in ECSA or particle growth in TEM, indicating a reasonably strong adhesion of Pt to the carbon support.

In this paper, we report for the first time a systematic study of the effects of ultrasound on the performance of the catalyst ink. ECSAs are compared for catalyst inks prepared in the absence (silent) and presence of ultrasound, at various ultrasonic frequencies, powers and exposure times. In this study and in our conditions, we observed a decrease in ECSA for catalyst ink samples when treated for longer irradiation times at the two ultrasonic frequencies employed. Herein, possible degradation mechanism(s) are proposed (assuming that the Nafion<sup>®</sup> is not affected by ultrasound).

Note that the authors have recently shown that ultrasonication of Nafion<sup>®</sup> solutions over various irradiation times revealed a decrease in viscosity. However, it was found that at a minimum ultrasonic time and a fixed ultrasonic frequency, an increase in Nafion<sup>®</sup> polymer viscosity was also observed. This observation was mainly attributed to the fact that depolymerisation caused by ultrasound, supplies new chain carriers for polymerisation, in other words under carefully chosen conditions, ultrasound may initiate polymerisation as previously observed in other studies using various polymers [10–16].

## 2. Experimental methods

### 2.1. Materials

In this study, two commercial catalysts were used as supplied by Tanaka Kikinokogyo (TEC10E50E; 45.9 wt% Pt/C TTK, Japan) and E-Tek (HP  $\sim 50$  wt% Pt/C, USA). Nafion<sup>®</sup> dispersion (10 wt%, EW 1100, D1021, DuPont), isopropanol (IPA, AR, Fisher) and ultrapure water ( $18.2 \text{ M}\Omega$  Millipore) were used for catalyst ink preparation. All gases used in these experiments were of ultra-high purity research grades (BOC, England).

### 2.2. Catalyst Inks preparation

The catalyst inks were prepared by mixing commercial Pt/C (C: Vulcan XC-72R) with Nafion<sup>®</sup> solution and IPA to form a

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