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Using Ultrasound to Effectively Homogenise Catalyst Inks: Is this Approach Still Acceptable?

Recommendations on the use of ultrasound for mixing catalyst inks

Bruno G. Pollet*§
Hydrogen Energy and Sonochemistry Research Group, Department of Energy and Process Engineering, Faculty of Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Torgarden, Norway

Shyam S. Kocha
Principal Consultant, Fuel Cells & Electrolyzers, Las Vegas, NV 89128, USA

***Email:** bruno.pollet@uqtr.ca

§Present address: GreenH2Lab, Pollet Research Group, Hydrogen Research Institute (HRI), Université Du Québec à Trois-Rivières (UQTR), 3351 Boulevard des Forges, Trois-Rivières, Québec G9A 5H7, Canada

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Since the early 2010s, less than a handful of studies have been communicated to the hydrogen and fuel cell communities that special care should be adopted, and a systematic approach should be applied, when homogenising catalyst ink slurries using ultrasound in the form of either a laboratory-grade ultrasonic cleaning bath, or an ultrasonic probe (sonifier). In these studies, it was demonstrated that the use of power ultrasound for the homogenisation of catalyst inks can be detrimental if not used appropriately. Unfortunately, and to this day, literature still indicates that ultrasound is still used for the homogenisation of fuel cell and electrolyser catalyst ink slurries and little or even no experimental conditions are given. To what extent is this approach acceptable? This short review paper discusses the importance of using ultrasound adequately to avoid catalyst dissolution and ionomer degradation induced by acoustic cavitation as well as metallic contamination originating from the ultrasonic probe. It also sheds some light on the important aspects and effects of power ultrasound in liquids and surfaces and presents some recommendations on how to use ultrasound adequately for mixing catalyst ink formulations.

1. Introduction

Low temperature fuel cells and electrolysers such as proton exchange membrane fuel cells (PEMFC), proton exchange membrane water electrolysers (PEMWE) and alkaline water electrolysers (AWE) are leading clean power conversion and hydrogen generation devices for the transport, stationary and industrial sectors. Anion exchange membrane fuel cells (AEMFC) and anion exchange membrane water electrolysers (AEMWE) are still at the research and development (R&D) stage, although significant advances have been achieved over the past 15 years, and component degradation has been identified as the limiting factor affecting their market deployment (1).

PEMFC, PEMWE and AEMWE contain membrane electrode assemblies (MEAs) where the electrochemical reactions take place. The MEA consists of a proton exchange membrane (PEM), catalyst layers (CL), gas diffusion layers (GDL), microporous layers (MPL) and transport porous

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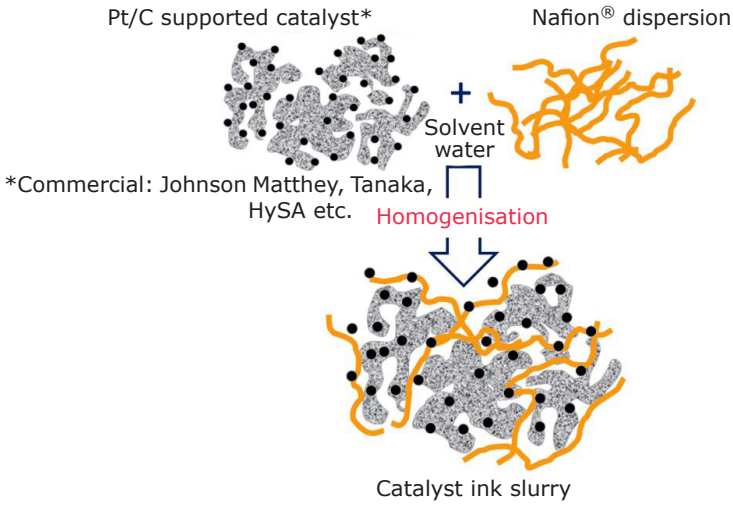

Fig. 1. Catalyst ink fabrication

layers (TPL). Typically, these components are produced individually and then pressed together at high temperatures and pressures. The electrodes are made of catalyst inks deposited either onto the GDL or the PEM leading to gas diffusion electrodes (GDE) and catalyst coated membranes (CCM) respectively. The catalyst ink is usually deposited by either the decal, blade process, screen-printing, painting, spraying (air and ultrasonic), electrospraying or electrophoretic methods (2–5).

There are numerous well-described methods detailing catalyst ink preparation, made for example of platinum supported on a high surface area (SA) and conductive carbonaceous material (for example, VULCAN® XC-72, Cabot Corporation, USA, Ketjenblack®) to yield platinum/carbon mixed with a solubilised polymer electrolyte (ionomer, such as Nafion®), a solvent (either 1-propanol or 2-propanol) and ultra-pure water (**Figure 1**). To obtain an efficient homogeneous catalyst dispersion, the catalyst inks are thoroughly mixed (2–5) either by magnetic stirring, by high-shear mixing (using a rotor-stator mixer at high rotation speeds), by ball-milling (also known as bead milling, a batch process in which a slurry is mixed with zirconia balls), by hydrodynamic cavitation (6) or by acoustic cavitation (ultrasonic agitation) (7–29).

Scientists and engineers in a typical research laboratory fabricating MEAs for fuel cell and water electrolyser applications, most often employ ultrasound for catalyst ink dispersion by either using a laboratory-grade ultrasonic cleaning bath, or an ultrasonic probe (sonifier) without paying attention of the ultrasonic frequency and acoustic power used, and more importantly to the effects of ultrasound on the catalyst ink components, particularly the catalyst and the ionomer. Generally, acoustic cavitation is neglected by the fuel cell and electrolyser communities. This is because this area of research has not been extensively explored, although a few studies exist (7–18), and the use of ultrasound in chemistry or sonochemistry is still seen as a niche R&D area (20–34). Moreover, in many cases, the literature does not report on: (a) the ultrasound source type and make, the ultrasonic frequency, acoustic power and ultrasonication time; and (b) the catalyst ink temperature, which is often not controlled or regulated during the experiment. In this short review paper, we will attempt to: (a) highlight the important aspects, advantages, and disadvantages of using ultrasound for the homogenisation of catalyst ink slurries; and (b) present some recommendations.

However, before considering the use and effects of ultrasound on catalyst ink slurries, a section on ultrasound and sonochemistry merits some attention.

2. Ultrasound and Sonochemistry

The use and application of ultrasound in chemical, physical and biological sciences can be divided into two distinct groups: (a) low frequency ultrasound or power ultrasound (20 kHz–2 MHz); and (b) high frequency ultrasound or diagnostic ultrasound (2–10 MHz) (30–34). Power ultrasound is regarded as the propagation and effect of an ultrasonic wave when transmitted through a liquid, leading to: (a) the creation of cavities (or voids) known as acoustic cavitation bubbles (microbubbles); as well as (b) acoustic streaming (29, 30).

Acoustic cavitation phenomena are usually associated with the formation, growth and collapse of cavitation bubbles induced by the propagation of an ultrasonic wave in a liquid, and consequently, to

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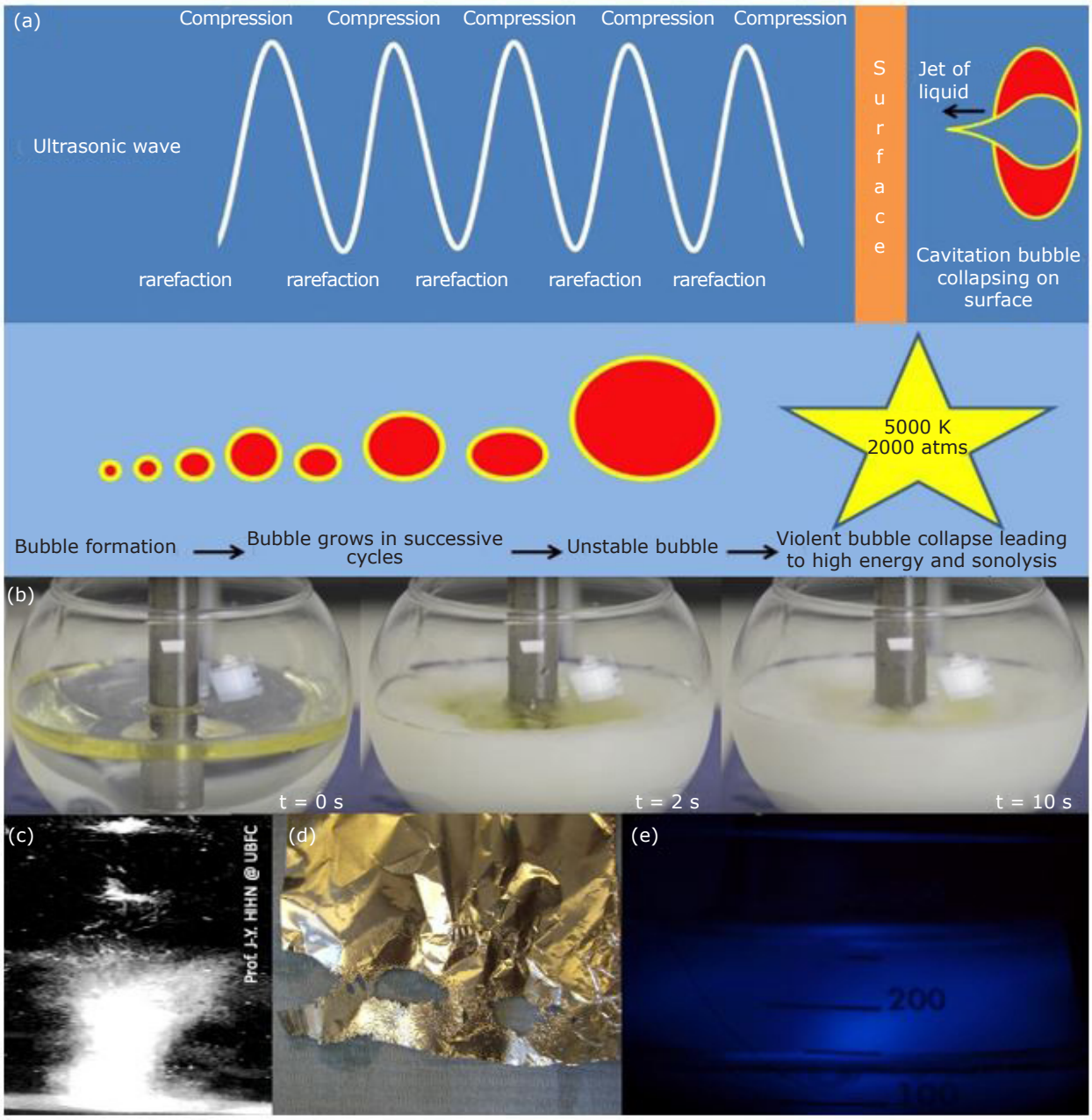

Fig. 2. Summary of the physical and chemical effects of ultrasound: (a) An ultrasonic wave propagating in a liquid, creating zones of rarefaction and compression, in turn producing cavitation bubbles, which upon implosion create high velocity jet of liquids towards a surface; (b) water/oil emulsification in the presence of ultrasound (probe, 20 kHz); (c) particle image velocimetry showing intense agitation close to the ultrasonic transducer (probe, 20 kHz – courtesy of Professor Jean-Yves Hihn, University Bourgogne Franche-Comté (UBFC), France); (d) effect of acoustic cavitation on a piece of aluminium foil ('kitchen foil') immersed for a few seconds in an ultrasonic cleaning bath (38 kHz); (e) ultra-fast imaging of a luminol (2 mM) solution subjected to ultrasound (probe, 24 kHz) placed in a dark cabinet (dark conditions, no visible light source)

the generation of very high pressures, shear stresses and temperatures, locally. At standard temperature and pressure, the collapsing of acoustic bubbles leads to the formation of microjets of liquid being directed towards the surface of the solid material (**Figure 2**) at speeds of up to 100 m s^{-1}. It is well-accepted in the field that cavitation bubble collapse leads to near adiabatic heating of the vapour that is inside the bubble, creating a so-called 'hotspot' in the liquid, where high temperatures (*ca*. 5000 K) and high pressures (*ca*. 2000 atms) are generated with a collision density of 1.5 kg cm^{-2} and pressure

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gradients of 2 TPa cm^{-1}, with lifetimes shorter than 0.1 µs and cooling rates above 10^{9-10} K s^{-1} during the collapse of cavitation bubbles.

Acoustic streaming can take place within three different regions: (a) in the bulk solution; (b) on the reactor walls; and (c) at the boundary layer. The power of acoustic streaming is directly proportional to the intensity of ultrasound, the SA of the ultrasonic emitting device and the attenuation coefficient of the medium. It is inversely proportional to the bulk solution viscosity and the speed of ultrasound (30).

Sonochemistry is a relatively new concept that received attention in the late 1970s and has been defined as the application of ultrasound in chemistry. In the late 1980s and early 1990s, the area was revived by Tim J. Mason (32) and Kenneth S. Suslick (34). A significant effect caused by acoustic cavitation is 'sonoluminescence' (33). Sonochemical reactions in an ultrasonic cleaning bath or with an ultrasonic probe (horn or sonifier) are most of the time subjected to transient elevated temperatures and pressures generated during cavitation bubble collapse. These cavitation bubbles usually contain gas molecules such as nitrogen and oxygen and vapour from the solvent. Here, water vapour is 'pyrolysed' into these 'microreactors' and dissociates to lead to the formation of extremely reactive species and other species such as hydroxyl radicals (OH•), hydrogen radicals (H•), hydroperoxyl radicals (•OOH) as well as hydrogen peroxide, ozone and oxygen atoms through endothermic chemical reactions (30, 33, 34) – a process known as sonolysis (Equations (i)–(iv)):

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \quad \text{(i)}$$

$$H^{\bullet} + HO_2^{\bullet} \rightarrow O_2 + H_2 \quad \text{(ii)}$$

$$H^{\bullet} + H_2O \rightarrow {}^{\bullet}OH + H_2 \quad \text{(iii)}$$

$$H^{\bullet} + H_2O_2 \rightarrow H_2 + HO_2^{\bullet} \quad \text{(iv)}$$

These species diffuse out from the interior of the bubble into the surroundings and react with solutes present in the aqueous solution (30). The hydroxyl radicals are the most dominant species in sonochemical reactions. Since the standard reduction potential for the redox couple $OH•,H^+/H_2O$ (+2.730 V *vs.* SHE) is much higher than that of H_2O_2/H_2O (+1.776 V *vs.* SHE) (35), OH• plays therefore a more critical role in sonochemical reactions than hydrogen peroxide. Near the bubble wall, the concentration of hydroxyl radical is usually in the micromolar and millimolar range and the lifetime of these are about 20 ns (30).

Overall, it is well accepted in the fields of power ultrasound and sonochemistry that ultrasonic waves propagating in liquids lead to acoustic cavitation, acoustic streaming, sonolysis (*in situ* radical generation), areas of extreme mixing close to the ultrasonic source (transducer), degassing, surface cleaning (and surface erosion) and significant rises in bulk temperature (especially at low ultrasonic frequencies). Ultrasonics are therefore often used for deagglomeration and for reducing particle size, dispersion, homogenisation and emulsification, especially in the case of catalyst ink preparation. **Figure 2** shows a summary of the physical and chemical effects of ultrasound.

3. The Use and Effects of Ultrasound on Catalyst Ink Slurries

In 2010, Takahashi and Kocha (7) described the importance of catalyst ink optimisation when evaluating PEMFC electrocatalyst activities towards the oxygen reduction reaction in liquid electrolytes. They highlighted the importance of producing good dispersion with the catalyst ink prior to deposition on carbonaceous or polymeric substrates to produce electrodes. In their study, good catalyst ink dispersions were qualitatively identified by ultrasonicating (ultrasonic bath; ultrasonic frequency and acoustic power not mentioned in the paper) the catalyst ink and allowing it to rest without mixing for a period. Electrochemical surface area (ECSA) was used as the quantitative parameter to decide whether the catalyst ink dispersion was optimal. In their study, they used several commercially available catalysts, namely, TEC10E50E (~46 wt% Pt/C), TEC10E50-HT (~46 wt% Pt/C-heat treated (HT)), as well as an alloy catalyst TEC36E52 (~46 wt% PtCo/C) from Tanaka Kikinzoku Kogyo (TKK, Japan).

The catalyst inks were prepared by mixing the catalyst powder with Nafion®, isopropyl alcohol (IPA) and ultra-pure water using ultrasound. They observed that the important factor in the catalyst ink optimisation was the ratio of the solvent (IPA) to water (found to be ~35%) in the catalyst ink formulation as well as the energy and duration of the subsequent ultrasonic treatment. They demonstrated that for a given catalyst ink composition, ultrasonication durations 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. Above 15 min and for up to 3 h, prolonged ultrasonication was found to produce no observable degradation in terms

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of loss in ECSA or particle growth in transmission electron microscopy, indicating a reasonably strong adhesion of platinum to the carbon support under these extreme conditions.

In 2014, Pollet and Goh (10) showed that the ECSA of a series of catalyst inks, made of commercial catalysts supplied by TKK (TEC10E50E, 45.9 wt% Pt/C) and E-Tek, USA, (HP ~50 wt% Pt/C) prepared in Nafion®, IPA and water, were affected by ultrasound (up to 40 kHz), acoustic powers (up to 12 W) and ultrasonic exposure durations (up to 2 h). Two types of ultrasonic systems were used, namely: a 40 kHz ultrasonic bath (375H, Langford Electronics Ltd, UK) and a 20 kHz ultrasonic probe (Vibra-Cell VCX 750 with a tip diameter of 6 mm, Sonics & Materials Inc, USA). They also showed that the mechanically shear-mixed (up to 19,000 rpm) catalyst inks were not affected by intense agitation, but longer ultrasonication times were detrimental to the catalyst ink composition and morphology, due to erosion (jets of liquid of high velocity, up to 400 km h^{-1} near the surface) and sonolysis phenomena induced by acoustic cavitation. It was observed that platinum nanoparticles were detached from the carbon support which led to a decrease in ECSA. It was speculated that a possible partial or complete platinum dissolution followed by an increase in the rate of platinum particle growth *via* Ostwald ripening and platinum agglomeration of platinum nanoparticles along with the action of Van der Waals forces occurred.

In later work, Shinozaki *et al.* (12) reported on the effect of cooling and type of ultrasonication, ultrasonication duration and power on the ECSA. They found that under ambient and ultrasonic conditions, heat was generated, and the temperature of the catalyst ink rose markedly leading to lower ECSA values by ~30%. They solved this issue by inserting the vials containing the catalyst inks in an ice-water ultrasonic bath during ultrasonication. In this set up, they observed smaller platinum nanoparticles and reproducible ECSA values. **Figure 3** shows the changes in ECSA, SA and mass activity (MA) for two types of ultrasonic systems (bath – FS30H, Fisher Scientific, UK, output: 42 kHz, 100 W – and probe – S-4000, Qsonica LLC, USA, output: 20 kHz, 600 W maximum), at various output powers in the absence and presence of ice-water. It was found that increasing the output power led to a significant decrease in the catalyst SA, MA and ECSA even when the catalyst ink was placed in an ice-water bath. To obtain efficient catalyst ink homogenisation and to avoid catalyst ink degradation, they concluded that an ice-water bath is required for catalyst ink preparation with an ultrasonic bath and ultrasonic probe (lowest power settings) operating at ultrasonication times of ~20 min and 30 s respectively.

In 2019, initial studies were followed up and deepened by Argonne National Laboratory, USA, and National Renewable Energy Laboratory, USA, by using ultra-small angle X-ray scattering (USAXS)–small angle X-ray scattering (SAXS)–wide-angle X-ray scattering (WAXS) (14). Wang *et al.* (14) confirmed previous studies (7, 10, 12) which showed that combining very short horn (probe) tip ultrasonication (SFX 250 digital sonifier (Branson Ultrasonics Corporation, USA), 250 W; micro tip diameter = 3 mm; ultrasonic frequency and acoustic power not mentioned in the paper) followed by bath ultrasonication (FS30, 100 W; ultrasonic frequency and acoustic power not mentioned in the paper) was found to be more effective in breaking up platinum agglomerates, yielding maximum catalyst activity and MEA performance. However, it was observed that

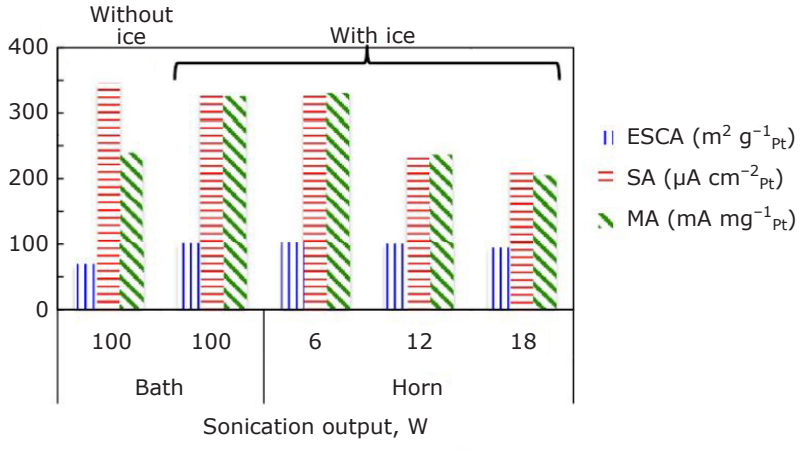

Fig. 3. Impact of cooling of catalyst ink using an ice-water bath during ultrasonication as well as ultrasonicator type and ultrasonication time on ECSA, SA and MA of platinum/high surface carbon fabricated using the Nafion®-free stationary air drying technique. Reproduced from (12) under Creative Commons Attribution 4.0 International (CC BY 4.0)

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prolonged ultrasonication was too destructive and led to platinum nanoparticle detachment from the carbon black support in turn yielding poor ECSA values and MEA performance.

Very recently Bapat *et al.* (15) introduced new tools and approaches to investigate simultaneously the dispersion state and stability characteristics of the mechanically stirred (no ultrasound – or 'silent' condition) and ultrasonicated catalyst inks. The catalyst inks were ultrasonicated using either an ultrasonic bath (Elmasonic S 10 (Elma Schmidbauer GmbH, Germany), 50/60 Hz, 30 W; ultrasonic frequency not mentioned in the paper) or an ultrasonic probe (SONOPULS HD 2200 (BANDELIN electronic GmbH, Germany), amplitude of up to 70%, sonotrode tip = 5 cm long, diameter = 13 mm; ultrasonic frequency not mentioned in the paper). The catalyst inks were also mixed using a magnetic stirrer (IKA Works GmbH, Germany, 50/60 Hz, 50 W) at 500 rpm over 24 h. They found that probe ultrasonication led to a highly stable catalyst ink (only up to an optimum ultrasonic amplitude).

A paper entitled 'A Comparison of Rotating Disc Electrode, Floating Electrode Technique and Membrane Electrode Assembly Measurements for Catalyst Testing' by Martens *et al.* (23) describes detailed testing protocols for characterising benchmarked and newly developed catalysts, for different laboratories to easily compare data. In this work, ultrasound in the form of an ultrasonic probe or a sonifier (either a BANDELIN Sonopuls HD 3200, a Branson Sonifier 150 or a Branson Digital Sonifier 450, with a 3 mm outer diameter horn tip) operating at the lowest ultrasonic power was used to disperse the catalyst homogeneously.

In these works, either the ultrasonic frequency, the acoustic power values or both were not mentioned; but more importantly the sonifier horn tip was immersed directly into the catalyst inks (7, 14, 23, 25, 26).

4. Contamination from the Sonifier Horn Tip

It is well-known in power ultrasound and sonochemistry that inserting the ultrasonic horn tip directly into the solution leads to sample contamination. It is because the probe, or more correctly the ultrasonic horn is often made of a strong and corrosion resistant titanium alloy, Ti-6Al-4V, which is unfortunately subjected to erosion due to acoustic cavitation at its surface.

For example, Mawson *et al.* (36) showed that the production of metallic micro-particulates (titanium, vanadium, aluminium (and iron)) from ultrasonic tip erosion occurred and was more pronounced at lower (for example, 18 kHz with power input of 180 W, UIP 1000, Hielscher GmbH, Germany, and 20 kHz with power input of 103 W, Branson Digital Sonifier Model 250, USA) than at high ultrasonic frequencies (2 MHz).

The Pollet group has recently shown (37) that the sonochemical production of platinum from platinum(IV) by direct immersion of the ultrasonic horn (20 kHz ultrasonic probe, 50% amplitude, 43 W acoustic power, 700 W maximum power output, 19 mm probe diameter, Q700, Qsonica) into the reaction vessel led to: (a) contamination of the reaction solution with micrometre size titanium, vanadium and aluminium on which platinum nanoparticles were deposited (**Figure 4**); and (b) a faster reduction of platinum(IV) in the presence of these contaminants and at longer ultrasonication times due to the constant supply of titanium-, vanadium- and aluminium-particles being eroded from the ultrasonic probe. It was observed that the gradual introduction of these impurities also resulted in faster reduction rates of platinum(IV) through heterogeneous nucleation. It was concluded that direct sonication at lower frequencies (such as 20 kHz) should therefore be avoided if the target catalytic material needs to be of high purity.

5. *In Situ* Radical Formation Induced by Ultrasonication

When using ultrasound, apart from neglecting the physical effects induced by acoustic cavitation, the chemical effects, such as sonolysis (*in situ* radical formation), are often not mentioned by the fuel cell and electrolyser communities. During sonolysis, it is known that water molecules are dissociated into hydrogen radicals (H•) and hydroxyl radicals (OH•) according to Equation (i). Ashokkumar *et al.* (38) found that in water, the concentration of OH• increased with increasing ultrasound frequency from 20 kHz to 358 kHz and, then for higher ultrasonic frequencies, for example above 450 kHz, the OH• yield drastically decreased. They attributed this observation to the fact that at higher ultrasonic frequencies (in the megahertz region), the acoustic cycles are extremely short,

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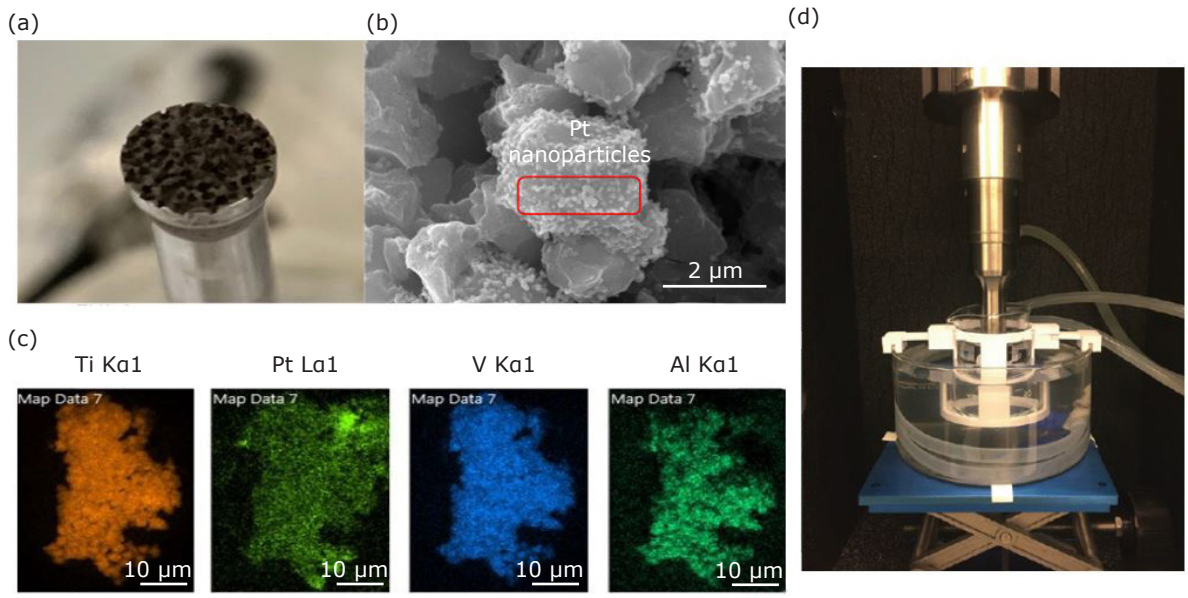

Fig. 4. (a) Photographic image of an ultrasonic horn which had operated for 40 min at 20 kHz (make, acoustic power); (b) scanning electron microscopy (SEM) image of impurity particles (titanium, vanadium and aluminium) on which platinum nanoparticles are deposited; (c) energy-dispersive X-ray spectroscopy (EDX)-maps of the same impurities and platinum; (d) sonochemical set up: direction ultrasonication by inserting the ultrasonic horn into the reaction vessel. Modified from (37) under Creative Commons Attribution-NonCommercial 3.0 Unported (CC BY-NC 3.0)

in turn limiting the growth and eventual collapse of the generated cavitation bubbles, and therefore affecting water sonolysis and OH• generation.

The presence of these sonolytic radicals could also trigger the sonochemical production of metallic nanoparticles (8). In (37), it was shown that the ultrasonication at two ultrasonic frequencies (20 kHz ultrasonic probe, 50% amplitude, 43 W acoustic power, 700 W maximum power output, 19 mm probe diameter, Q700, Qsonia – 408 kHz ultrasonic bath, 100% amplitude, 54 W acoustic power, Honda Ultrasonics, Japan) of 2 mM of platinum(IV) chloride in 0.8 M 96% ethanol and Milli-Q water led to the formation of platinum(0) without the use of a chemical reducing agent (for example, sodium borohydride). **Figure 5** shows the concentration of platinum(IV) in the solution as a function of ultrasonication time under 20 kHz and 408 kHz. The size of the nanoparticles synthesised sonochemically at ultrasonic frequencies of 408 kHz and 20 kHz were found to be 1.4 nm and 2.7 nm respectively, while the nanoparticles synthesised through sodium borohydride reduction were found to be 4.1 nm. Therefore, the sonochemical synthesis produced nanoparticles of smaller crystallite sizes than the chemical reduction method, which was possibly due to the deagglomeration induced by ultrasonication and higher cavitational events at that ultrasonic frequency. From the findings, it

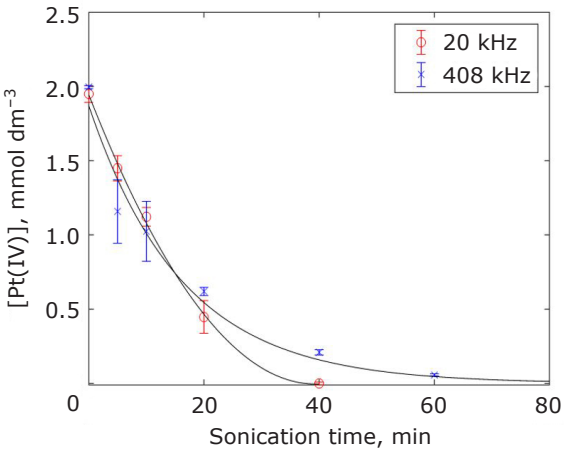

Fig. 5. Concentration of platinum(IV) in solution as a function of ultrasonication time under 20 kHz and 408 kHz. Reproduced from (37) under Creative Commons Attribution-NonCommercial 3.0 Unported (CC BY-NC 3.0)

was clear that ultrasonication leads to complete reduction of Pt^{4+} in as short as 40 min of reduction time, *via* Equations (v) and (vi):

$$H_2O \text{))))) } H\bullet + OH\bullet \quad (v)$$

$$Pt^{4+} + \text{reducing radicals} \rightarrow Pt(0) \quad (vi)$$

Early preliminary results (not shown here) on 30 min ultrasonication (40 kHz ultrasonic bath,

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acoustic power = 8 W) of a catalyst ink (prepared following (39)) containing a commercial Pt/C in Nafion®, IPA and ultra-pure water using a laboratory ultrasonic bath, indicated that dissolved platinum concentration (monitored by single particle inductively coupled plasma, *sp*-ICP-MS) decreased significantly up to 10 min ultrasonication and then increased until 30 min (below the initial platinum concentration at $t = 0$). The possible explanation for this observation could be due to the reduction Pt^{4+} to Pt^0 then followed by a partial platinum dissolution caused both sonolysis and acoustic cavitation. This speculative argument may explain these early observations and a full and systematic study is currently underway.

6. The Effect of Ultrasound on a Carbon-Based Substrate

The use of ultrasound in the generation and modification of carbon-based materials, for example mesoporous and macroporous carbon micro/macro-particles, carbon nanotubes (CNT), and graphene and graphene oxide dispersions has been studied (40). In these investigations, ultrasound has been shown to be very useful in scattering and solubilising CNT as well as directly functionalising their surfaces by breaking the C=C double bonds in the presence of strong acids (40). It has also been shown that ultrasonicated carbon-supported mono- and bi-metallic catalysts yielded excellent electrochemical activity due to surface functionalisation of the carbonaceous support and better dispersion induced by ultrasound (8). In a detailed study, Sesis *et al.* (41) showed that acoustic cavitation leads to chemical modification of the CNT surface and helps CNT exfoliation and length reduction, and efficient dispersion of CNT in aqueous solutions is mainly due to mechanical forces. To this date and from the authors' knowledge, there have been no detailed studies on the effects of ultrasound on highly conductive carbon blacks of turbostratic structures with high SAs as support materials for fuel cell and electrolyser catalysts, such as VULCAN® XC-72R (250 $m^2\ g^{-1}$), Shawinigan Black (Chevron Phillips Chemical, USA, 80 $m^2\ g^{-1}$), BLACK PEARLS® 2000 (Cabot Corporation, 1500 $m^2\ g^{-1}$), Ketjenblack® (Ketjenblack® EC-600JD and Ketjenblack® EC-600J Ketjen International, 1270 $m^2\ g^{-1}$ and 800 $m^2\ g^{-1}$ respectively) and DENKA BLACK (Denka, Japan, 65 $m^2\ g^{-1}$) (8).

7. Does Ultrasound Affect the Ionomer?

Power ultrasound is also used for polymerisation and depolymerisation in polymer chemistry as it causes atomisation, molecular degradation as well as chemical rate and yield improvement. However, it has also been demonstrated in numerous studies that power ultrasound can greatly enhance the decomposition and degradation of some polymers due to the formation of radicals induced by sonolysis (42–46). Power ultrasound is now regarded as a powerful method for the depolymerisation of macromolecules, usually observed in the reduction of the polymers' molecular weights, mainly caused by acoustic cavitation (45, 46). In all these studies, long-time ultrasonic irradiation of the polymer led to a permanent reduction in solution viscosity, which was in most cases, irreversible (46).

The Holdcroft (16) and Pollet research groups (9, 16) undertook systematic investigations that were performed to shed some light on the effects of power ultrasound on a series of Nafion® ionomer dispersion concentrations under various ultrasonication durations at 42 kHz (acoustic power = 2.1 ± 0.2 W, 1510 Ultrasonic Cleaner, Branson Ultrasonics Corporation) and using a simple laboratory ultrasonic cleaning bath. They found that, under controlled bulk solution temperature (298 K), as the ultrasonication irradiation duration increased, the Nafion® dispersions' viscosity decreased; however, this effect was more evident for all samples treated under unregulated bulk solution temperature and lower dispersion concentrations. For these samples, mass loss was observed possibly due to a more defined cleavage of the acidic side chains.

From these early studies, in 2020, Safronova *et al*. (17) showed that ultrasonic treatment (35 kHz ultrasonic bath, ultrasonic power = 4 W, BANDELIN electronic GmbH) of Nafion® polymer solutions led to: (a) an increase in proton conductivity of membranes obtained *via* casting procedure up to 40% after ultrasonication for 30–45 min; and (b) a deterioration of the mechanical properties as compared with the initial membrane. Very recently, Safronova *et al.* (18) also demonstrated that ultrasonication (20 kHz ultrasonic probe, ultrasonic powers = 2.7–9.4 W, Vibra-Cell VSX 130, Sonics & Materials Inc) of Nafion® polymer solutions affected the microstructure and transport properties of the resultant membranes due to the improvement of the connectivity of pores and mobility of charge carriers.

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The ultrasonic treatment resulted in both an increase of conductivity and a decrease in the selectivity of cation transfer in recast Nafion® membranes.

8. Important Parameters, Ultrasonic Equipment and Glassware

8.1 Effect of Temperature Induced by Ultrasonication

It is well known that low frequency ultrasound yields rapid temperature rises within the solution with Δ*T*s of up to ~+50ºC in short exposure times starting from room temperature. In other words, the bulk solution 'heats' up. Although this can benefit endothermic reactions as well as reaction kinetics, some issues may arise regarding data reproducibility. It is therefore important that the bulk temperature is carefully regulated and controlled during ultrasonication to separate the effects of acoustic cavitation from temperature effects. Moreover, a fast temperature rise often leads to volatilisation of the analyte (water, organic solvent) in other words to molecular degradation. In addition, as the temperature is increased, the physical characteristics of the solution are affected, and no acoustic cavitation is observed — this phenomenon is known as the 'decoupling effect'. In the case of catalyst ink homogenisation and in the literature, ultrasonic time is stated and varies from 5 min to 24 h ultrasonication from one study to another.

Temperature during ultrasonication has therefore a major effect on the homogenisation efficiency through increased vapour pressure and changes in solvent and bubble dynamics. There are several strategies to control the ultrasonicated the catalyst ink slurry. The first is to use an ice bath (to ensure rapid heat dissipation), in which the glass vessel containing the catalyst ink slurry is inserted. Although a simple method, the main issue is that the ultrasonic energy is absorbed by the ice, and thus, the ice needs to be replaced if longer ultrasonication times are applied. The second option is to use specially designed reactor cells, for example, coolant-jacketed cells (linked to a thermostatic bath or a cryostat), and the third is to use the 'pulse' mode of ultrasonication (only available in newer ultrasonic systems).

8.2 Sonochemical Efficiency

In order to assess the sonochemical effects of an ultrasonic system, the sonochemical efficiency (SE, in mol J^{-1}) is often calculated. SE is an important parameter as it allows for a direct comparison of the sonochemical data between different ultrasonic systems and thus, the ultrasonic frequency is the only parameter responsible for any differences in the SE between the various setups.

For such a SE calculation, the acoustic power (watts) and radical (OH•) formation rate (mol s^{-1}) need to be determined. However, determining the sonochemical formation of radicals (H• and OH•) in an aqueous solution during ultrasonication is rather challenging due to the very short lifespan of the radicals. There are several chemical dosimetry methods, namely the terephthalic acid, Fricke and Weissler methods, for measuring the hydrogen peroxide or OH• formation during ultrasonication. In the case of acoustic powers, they are often determined by the calorimetry method. For further information on how to calculate the SE, the reader is invited to consult (11, 37).

8.3 Electrical Power vs. Acoustic Power

From the literature, some confusion exists between the electrical power ($P_{electrical}$, in watts) and the acoustic power ($P_{acoustic}$, in watts) from an ultrasonic system. The electrical power is the power delivered to drive the ultrasonic transducer. The acoustic power is the rate at which the ultrasonic energy is transmitted to the liquid per unit time. Although it is rather straightforward to measure the consumable electrical power, it does not represent the power of the cavitational process. To determine the efficiency of a sonochemical process, the amount of acoustic energy introduced and transmitted in the liquid must be determined. It is well known in the field that only a portion of the acoustic energy is active in the process under study and a part of the irradiated but unabsorbed acoustic energy must not be considered. For these reasons, the yield in sonochemical process must be related to the acoustic energy absorbed in a fixed volume of liquid rather than the irradiated power. One appropriate method to determine acoustic power is the calorimetric method. In this method, one assumption is that all the absorbed acoustical energy is transmitted into heat. The main idea of this method is the continuous recording of the temperature change with time during ultrasonication. For further information on how to determine the acoustic power, the reader is invited to consult (11, 37).

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9. Ultrasonic Equipment

9.1 Ultrasonic Cleaning Bath

The ultrasonic cleaning bath is the most widely available source of ultrasonics in scientific and engineering laboratories and workshops. The ultrasonic frequency and acoustic power of an ultrasonic cleaning bath depends upon the type and number of transducers used in its construction. Some newer ultrasonic baths have adjustable 'acoustic' power, ultrasonic pulse modes and built-in thermostatic heaters. Ultrasonic bath systems have the advantages of being widely used and inexpensive, and a fairly good temperature control when compared with ultrasonic probe systems. However, they suffer from a low transmitted ultrasonic power into the reaction vessel, a fixed ultrasonic frequency is often used and the positioning of the reaction vessel in the ultrasonic bath affects the consistency on the generated data, which is related to the acoustic power.

9.2 Ultrasonic Probe

To increase the level of acoustic energy available to a solution, it is necessary to introduce the ultrasonic source directly into the liquid as a large ultrasonic intensity (acoustic power divided by the vibrating tip area, in watts per cm^2) can be achieved at the radiating tip. The ultrasonic frequency range used in R&D laboratories is of the order of 20–100 kHz. Probe systems offer advantages and disadvantages over bath systems. The main advantages are as follows: (a) much higher ultrasonic powers can be used since energy losses during the transfer of ultrasound through the liquid and the reaction vessel walls are eliminated; (b) the system can be tuned to give optimum performance in the reaction vessel for a range of acoustic powers; and (c) the acoustic power and size of the sample to be irradiated can be matched accurately for optimum effect. However, they also suffer from: (a) tip erosion which can cause contamination by the released titanium alloy micro/nanoparticles during ultrasonication; (b) fixed ultrasonic frequency; (c) difficulty in controlling the temperature; (d) high generation of radical species in the vicinity of the vibrating tip; and (e) they are costly. Indeed, the ultrasonic probe suffers from high and fast temperature rises, although this problem can be alleviated to some extent in modern instruments by the incorporation of a pulse mode of operation or by carefully controlling the temperature (see next section).

9.3 Glassware for Ultrasonication

Specially designed glassware is usually employed when performing ultrasonic experiments to: (a) control and regulate the temperature; (b) avoid contamination arising from the ultrasonic probe; and (c) improve data repeatability. Two types of glassware or so-called 'sono-reactors' in the field are used in which: (a) the ultrasonic flat transducer (**Figure 6(c)**) or probe (**Figure 6(b)**) is inserted at the bottom the cell (called the 'face-on'

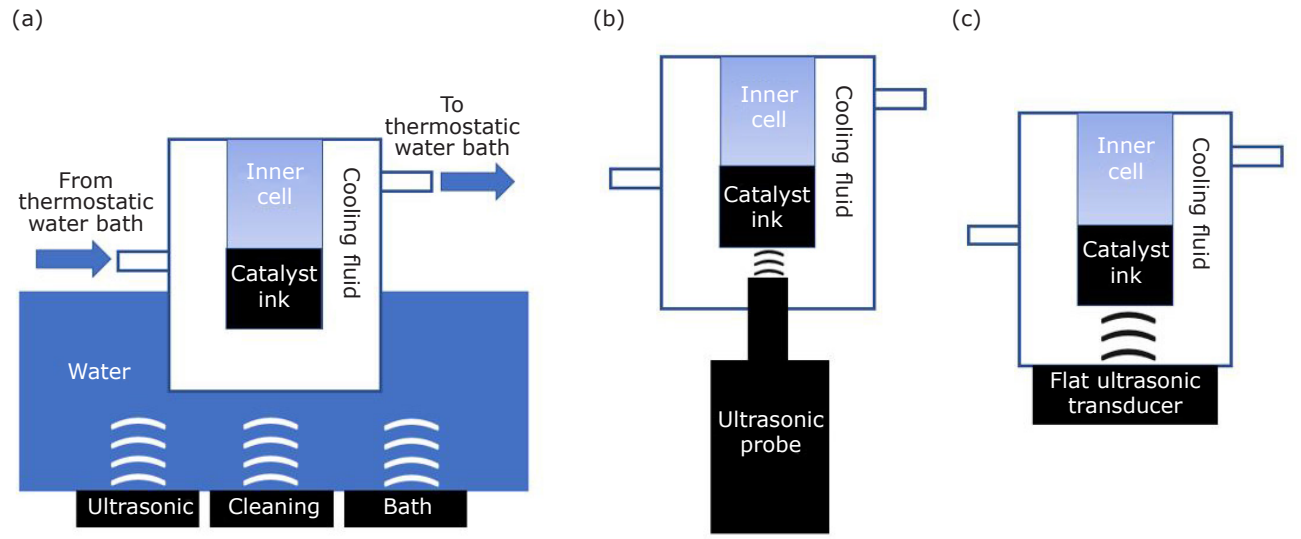

Fig. 6. (a) Thermostatically regulated reaction cell placed directly in the ultrasonic bath; (b) thermostatically regulated reaction cell with the ultrasonic probe in a 'face-on geometry'; (c) thermostatically regulated reaction cell integrated with a flat ultrasonic transducer

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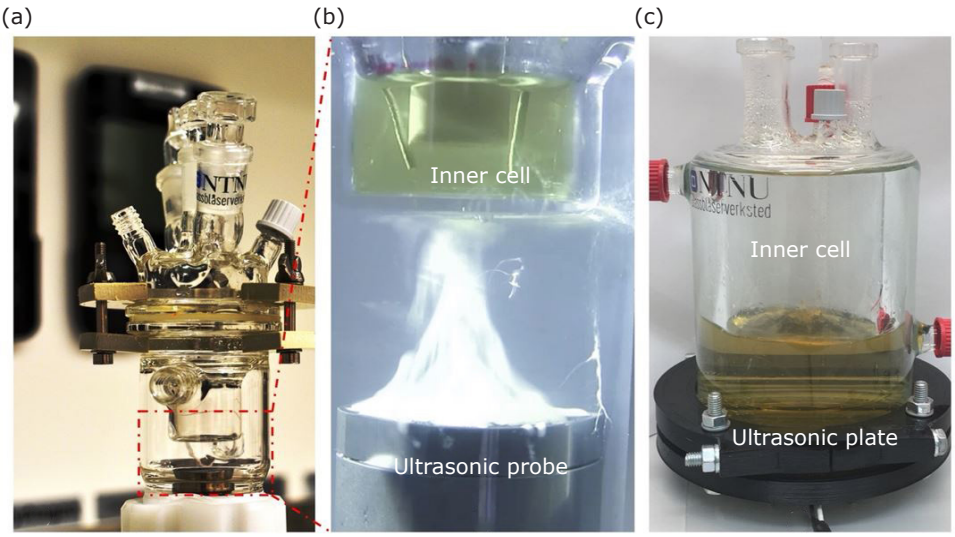

Fig. 7. (a) A double-jacketed sono-reactor with an inner cell (*V* = 10 ml) in a 'face-on geometry'; (b) a close-up view of the ultrasonic probe (26 kHz) and inner cell; (c) a 488 kHz ultrasonic reactor with an inner cell (*V* = 100 ml)

geometry); or (b) the cell is directly immersed in the ultrasonic cleaning bath (**Figure 6(a)**). These sono-reactors are double-jacketed to allow a coolant to circulate from a thermostatic bath or cryostat, and the inner cell in which the solution is inserted. A flat bottom inner cell or outer cell (**Figure 7**) is used to maximise energy transfer, as the acoustic energy is transferred vertically from the base of the ultrasonic bath or transducer and through the glass walls of the inner cell into the solution itself.

10. Other Homogenisation Methods

Apart from using acoustic cavitation for effective homogenisation (7–29), there are other methods for thoroughly mixing (2–5) the catalyst inks by either magnetic stirring, ball-milling, hydrodynamic cavitation or high-shear mixing (6, 47–49). For all techniques, studies on the effect of high shear mixing on the performance of catalyst ink slurries are scarce. High shear mixing appears to be a technique that is used in some laboratories for homogenising catalyst ink slurries. It involves using a high-shear mixer (such as Silverson, Heidolph, IKA) containing a metallic rotating blade operating at rotation speed up to 20,000 rpm (10, 13, 14). Fairly recently, Jacobs (13) showed that high shear mixed catalyst inks are more effective at higher stirring rates as high mixing energies lead to effective production of catalyst/Nafion® interfaces, in turn improving the so-called 'three phase boundary' observed during *in situ* fuel cell testing.

11. Hydrodynamic Cavitation Method: A Possible Solution!

Two types of cavitation exist: acoustic cavitation and hydrodynamic cavitation. The latter is caused by flowing liquid static pressure drops and, as the liquid flow passes through constricted geometries (for example, an orifice plate, a venturi or a throttling valve), the flow rate increases and in turn a decrease in static pressure is observed. When the pressure drops below the local saturated vapour pressure, cavitation nuclei present in the liquid start to grow as their internal pressures become greater than their surface tensions. Eventually they become unstable as soon as the flow pressure recovers and then implode by creating jet of liquids of high velocity (48, 49). In hydrodynamic cavitation, the resultant bubble collapse intensity is low compared to acoustic cavitation. But in terms of developing a large-scale system, it is comparatively easy (tank, pump, control valve and pipes/tubing) and maintenance is also easy. For acoustic cavitation, the acoustic field is usually not uniform when the size of the reactor increases (in terms of diameter as well as length) and hence uniform cavitation field is difficult to obtain. Overall, effective cavitation regime is reduced, although the collapse intensity of the bubbles is high.

In general, for achieving the desired physical effects (mixing, dispersion, extraction, cleaning, homogenisation, deposition, coating) acoustic and hydrodynamic methods are powerful and in terms of energy efficiency, hydrodynamic cavitation is better (see **Table I** (49)). From experience, the

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Table I Energy Efficiency of Cavitation Equipment. Modified from (49)

Equipment	Hydrodynamic cavitation	
	Energy efficiency, %	**Flow rate, $m^3 h^{-1}$**
Centrifugal pump (low pressure)	50–70	>10
Displacement pump (high pressure)	20–40	<10
Equipment	**Acoustic cavitation**	
	Energy efficiency, %	**Acoustic power, W**
Low frequency ultrasound <1 MHz	45–70 <45	<200 200–1000
Low frequency ultrasound <2 MHz	70	<1

hydrodynamic cavitation method is superior for physical effects whereas acoustic cavitation is more suitable for chemical effects (especially when scaled up).

In 2019, for the first time, Kuroki *et al.* (6) used the hydrodynamic cavitation method to efficiently disperse PEMFC catalyst ink slurries. In their experimental set up, the catalyst slurry was subjected for 30 min to hydrodynamic cavitation bubbles generated by rotating the impeller in a centrifugal pump at a frequency of 80 Hz (ω = 4800 rpm) operating at ~1.3 kW power output. They also used the batch-type ball-milling method, produced the electrodes (CCM prepared by the decal method)/MEAs and carried out the PEMFC testing. They found that MEAs prepared using catalyst ink dispersed by hydrodynamic cavitation and ball-milling methods exhibited higher fuel cell performance than those prepared by the ultrasonication method (**Figure 8**). They suggested that the insufficient dispersion of platinum/carbon catalyst ink slurries was due to the poor breakup of the catalyst agglomerates (mainly from carbon) and cracks on the CCM surface during

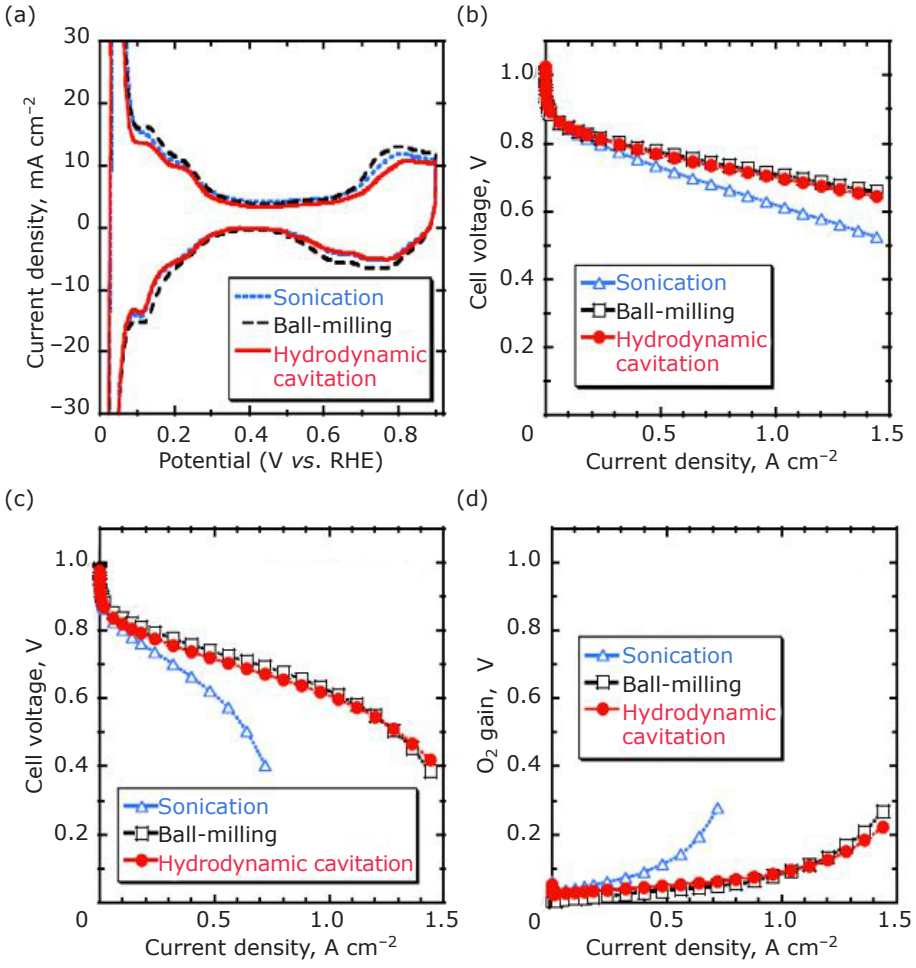

Fig. 8. (a) CV curves IV curves at 80ºC for: (b) hydrogen/oxygen; and (c) hydrogen/air operation; and (d) oxygen gain for the MEAs prepared using three different dispersion treatments on the catalyst slurries. Reproduced from (6). Copyright (2019) American Chemical Society

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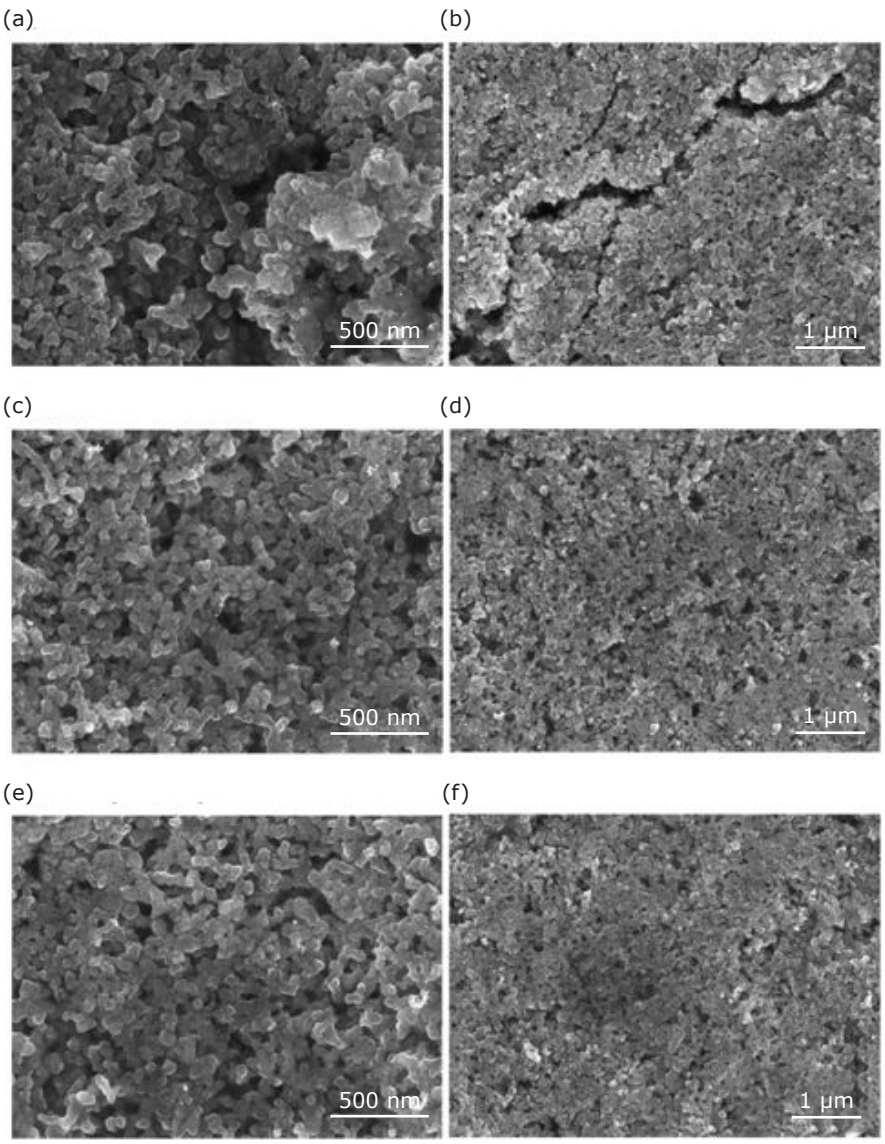

Fig. 9. SEM images of the CL on the membranes prepared using the dispersion treatments of (a) ultrasonication at 500 nm; (b) ultrasonication at 1 µm; (c) ball-milling at 500 nm; (d) ball-milling at 1 µm; (e) hydrodynamic cavitation at 500 nm and (f) hydrodynamic cavitation at 1 µm on the catalyst slurries. Reproduced from (6). Copyright (2019) American Chemical Society

ultrasonication leading to an unfavourable pore structure for oxygen transport in the CL (**Figure 9**).

12. Recommendations

The answer to the question of this short review paper title is: "Yes, the approach is still acceptable", however special care and great attention should be taken before performing the ultrasonic experiments. We recommend the following:

- A specially designed double-jacketed glassware vessel (sono-reactor) should be used if ultrasonic cleaning bath and ultrasonic probe systems are to be employed. The inner reactor solution temperature should be controlled, regulated and maintained by either a thermostatic bath or a cryostat
- The ultrasonic cleaning bath should have the right level of water and the sono-reactor should be placed in the middle of it and with its base being at a depth of ~1 cm. It is important to note that the acoustic power output from an ultrasonic cleaning bath differs from one to another. Moreover, the positioning of the sono-reactor in the ultrasonic cleaning bath is important as the acoustic power varies greatly within the same bath
- To ensure that the ultrasonic cleaning bath is working properly i.e., it produces acoustic cavitation, a very simple experiment should be performed by placing a piece of aluminium foil in the bath and leaving it for a few seconds to see whether perforations occur, i.e., pinholes are observed
- Direct ultrasonication by means of an ultrasonic probe should be avoided to eliminate

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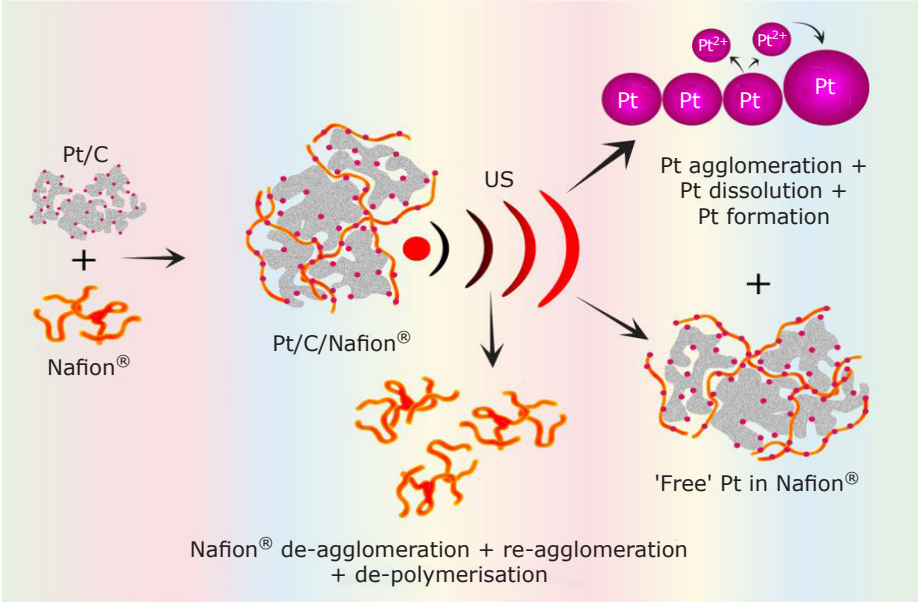

Fig. 10. A graphical summary of the effects of ultrasound on the catalyst ink slurries

contamination from the vibrating tip
- The acoustic power should be determined by, for example, calorimetry (see (8) for instructions) by simply using water in the inner cell
- The ultrasonic equipment, ultrasonic frequencies, acoustic powers and durations as well as the catalyst ink temperature should be reported in investigations using ultrasound
- From our investigations and experience, shorter irradiation times should suffice to obtain very good catalyst ink homogenisation and dispersion for example, 10 min using a 20 kHz ultrasonic probe and up to 30 min using an ultrasonic cleaning bath (in the region of 40 kHz)
- If catalyst ink dispersion needs to be scaled up and energy cost is an issue whilst ensuring effective homogenisation and minimising catalyst ink slurry deterioration, the hydrodynamic cavitation method could be a possible solution. Although process optimisation at laboratory scale would need to be carried out.

13. Conclusions

Low frequency ultrasound provided by either an ultrasonic cleaning bath or an ultrasonic probe involve acoustic cavitation, in which cavitation bubbles are created. When these bubbles grow in size, they become unstable and then violently collapse creating localised transient high temperatures and pressures, together with the formation of a high velocity jet of liquids directed to surfaces (mainly responsible for surface erosion and activation). Catalyst ink dispersion is an important factor if better fuel cell and electrolyser catalyst utilisation and thus performance are to be achieved. There are various methods that are being used to efficiently homogenise catalyst ink slurries, such as magnetic stirring, high-shear mixing, ball-milling, hydrodynamic cavitation and acoustic cavitation (ultrasonic agitation). The latter method has been extensively used in fuel cell and electrolyser laboratories, as most of them possess cheap and available ultrasonic cleaning baths. However, ultrasound should be used appropriately and with great care to avoid catalyst dissolution and ionomer degradation induced by acoustic cavitation as well as metallic contamination originating from the ultrasonic probe. Moreover, for laboratory and data comparison purposes, the ultrasonic equipment (and make), ultrasonic frequencies, acoustic powers, ultrasonication durations and sonochemical efficiencies need to be clearly reported. **Figure 10** shows a graphical summary of the effects of ultrasound on catalyst ink slurries.

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The Authors

Professor Bruno G. Pollet (h-index = 47, ~9000 citations) is a Professor of Chemistry at the University of Québec at Trois-Rivières (UQTR) and Deputy Director of the UQTR Research Hydrogen Institute (HRI). He currently leads the Green Hydrogen Lab. He is a Fellow of the Royal Society of Chemistry (RSC) and he is President of the Green Hydrogen division of the International Association for Hydrogen Energy (IAHE). His research covers a wide range of areas in electrochemistry, electrochemical engineering, sonoelectrochemistry and energy materials. He was a full Professor of Renewable Energy at the Norwegian University of Science and Technology (NTNU), a full Professor at the University of the Western Cape, South Africa, and R&D Director of the National Hydrogen South Africa (HySA) Systems Competence Centre. He was a co-founder and an Associate Director of The University of Birmingham Centre for Hydrogen and Fuel Cell Research, UK. He has worked for Johnson Matthey and other various industries worldwide as Technical Account Manager, Project Manager, R&D Manager/Director, Head of R&D and Chief Technology Officer (CTO). Bruno is member of several editorial boards of international journals (Elsevier, RSC, Springer and Wiley).

Shyam S. Kocha (h-index = 36, ~11,000 citations) is an independent consultant working with start-ups and automotive companies in the areas of fuel cells and electrolysers. As a consultant to various projects, he provides clients with technical advice on fundamental and applied areas of electrochemical evaluation of materials, components and devices as well as diagnostics to improve performance and durability and lower costs. He has ~20 years' experience in fundamental and applied electrochemistry in the automotive PEM fuel cells industry (United Technologies, USA, General Motors, USA and Nissan, Japan) and at the National Renewable Energy Laboratory (NREL, USA). He has led fuel cell R&D teams in platforms ranging from half-cells to short stacks, automotive fuel cell modules and fuel cell vehicle durability analysis andmitigation. He was thrust leader for 'Electrode Layer Integration' for PEMFCs as part of the United States Department of Energy (USDOE) Office of Energy Efficiency and Renewable Energy (EERE) Fuel Cell Performance and Durability (FC-PAD) consortium consisting of five national labs, National Renewable Energy Laboratory (NREL), Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), Lawrence Berkeley National Laboratory (LBNL) and Argonne National Laboratory (ANL)) and several industrial (General Motors, 3M, and Ford, USA) and academic partners. His recent work with start-ups includes alkaline reversible fuel cells as well as electrolysers based on CO_2 reduction to fuels.

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