NPL Report MAT 114

Challenges in Realising
Composite Liquid Hydrogen Cryogenic Storage:

A Materials and Standards Perspective

S Giannis, N Salmeron Perez, N Spetsieris

January 2023

Challenges in Realising Composite Liquid Hydrogen Cryogenic Storage: A Materials and Standards Perspective

S Giannis, N Salmeron Perez, N Spetsieris

Department of Materials and Mechanical Metrology
Science & Engineering Directorate

ISSN: 1754-2979

DOI: https://doi.org/10.47120/npl.MAT114

National Physical Laboratory

Hampton Road, Teddington, Middlesex, TW11 0LW

This work was funded by the UK Government’s Department for Business, Energy and Industrial Strategy (BEIS) through the UK’s National Measurement System programmes.

Approved on behalf of NPLML by

Kevin Blakley, Group Leader - Advanced Engineering Materials

Executive Summary

Hydrogen is an energy vector that has great potential to provide a viable solution for meeting climate challenges. A key element in an end-to-end hydrogen supply chain is storage that can be as a compressed gas or as a cryogenic liquid. Only high pressure compressed gaseous hydrogen offers a similar energy density to cryogenic liquid hydrogen at moderately low pressures. The latter offers the possibility of reducing the storage container mass and volume, however, requires the hydrogen to be cooled to a temperature of approximately -253 °C.

The transportation industry (air and land in particular) is keen in utilising hydrogen as fuel as it does not produce any carbon emissions during combustion. However, for commercially viable, large commercial aircraft the hydrogen needs to be stored cryogenically as a liquid. Similarly in heavy-duty land vehicle applications, storing hydrogen onboard the vehicle as a cryogenic liquid can increase the range of the vehicle by a factor of 1.5 to 2 compared to the hydrogen gas unit being replaced.

However, there are barriers associated with realising liquid hydrogen cryogenic storage, particularly when utilising lightweight polymer composite materials essential for applications like on-board vehicle storage.

Specifically, whilst at the top-end of the regulatory framework (Regulations) existing regulations for pressure equipment safety and carriage of dangerous goods and use of transportable pressure equipment, provide the legal framework for cryogenic liquid storage, the available technical standards are prescriptive and at present allow mainly for metallic materials to be utilised for the storage container. Having said that, available standards developed via the International Standards Organisation Technical Committees 'ISO/TC 220 Cryogenic vessels' and 'ISO/TC 58 Gas cylinders' provide a satisfactory framework that can be expanded to other materials and systems.

In the case of storage of liquid hydrogen as fuel onboard a vehicle, there is a gap left at the top of the regulatory framework with the recent repealing of Regulation (EC) 79/2009 and the narrower scope of UN/ECE Regulation No. 134 and several components critical for a hydrogen-powered vehicles were left with no applicable type-approval framework. As far as technical standards are concerned, 'ISO/TC 197 Hydrogen technologies' has published a document , ISO 13985:2006, which specifies the construction requirements for refillable fuel tanks for liquid hydrogen used in land vehicles, as well as the test methods required to ensure that a reasonable level of protection from loss of life and property resulting from fire and explosion is provided. The standard allows for the use of non-metallic materials, however further developments in measurement standards at cryogenic temperatures are required for this to be fully realised.

There is a significant body of primarily academic literature referring to the cryogenic performance of composite materials that has been produced over the last 30 years or so. The main class of polymer matrix composites studied have been thermoset based, although some thermoplastic systems have been covered. Materials have been characterised down to temperatures as low as 4K and properties including mechanical (tension, compression, flexure, fracture toughness etc.), thermal (thermal expansion,

thermal conductivity) and physical (permeability characteristics) have been measured. Reported material properties show a high level of variability which can be largely attributed to the lack of validated measurement methods for composites at cryogenic temperatures.

A half-day virtual workshop was organised by the National Physical Laboratory focusing on cryogenic materials, properties and standards. The comprehensive discussion revealed that in addition to gaps in regulations, technical and measurement standards, there are also significant gaps in the measurement infrastructure itself. It was thought that temperature verification approaches, uncertainty of strain measurement systems as well as suitability of existing jigs and fittings being key for realising validated and trusted material properties data. The workshop attendees agreed that an Advisory Group to bring the community together would be extremely beneficial and could act as the springboard for the establishment of a future Joint Industry Project (JIP) to tackle generic cryogenic measurement issues across a range of industry sectors and applications.

Contents

1 Background and Industry Drivers

Introduction

The motivation for this study was the recent increasing demand from material suppliers, designers and original equipment manufacturers (OEMs) to establish an understanding of the cryogenic performance of engineering materials and in particular fibre-reinforced polymer (FRP) composites. This is primarily driven by hydrogen and its use as a source of energy on a large scale (Figure 1). Hydrogen (H_2) is an energy vector that has shown great promise worldwide as a solution for meeting climate challenges. This is because it is able to store and produce large quantities of energy per unit mass without creating carbon emissions during combustion.

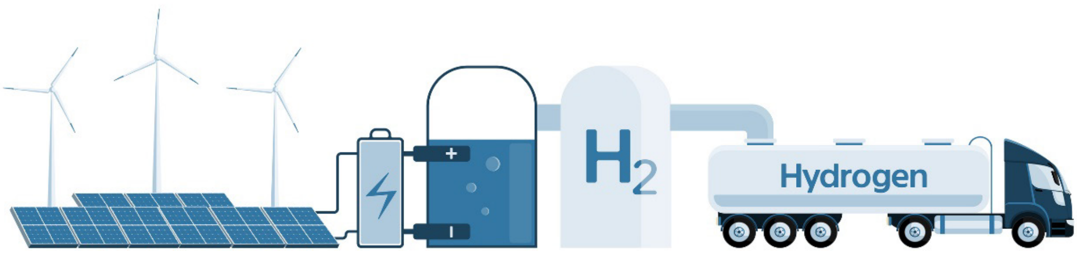

Figure 1. Hydrogen production, storage and distribution

A key element in an end-to-end hydrogen supply chain is storage that can be either as a compressed gas or as a cryogenic liquid. It is the latter application that requires materials qualification at extremely low temperature conditions. This study therefore focusses on hydrogen storage as the use case for exploring aspects of the measurement infrastructure that are required to effectively characterise the cryogenic performance of FRP composites, particularly through the lens of associated regulations, design codes and measurement standards.

The study initially identifies the requirements for hydrogen storage and the industry drivers before deep diving into the regulatory framework and the associated technical standards. Furthermore, a comprehensive literature survey has been conducted to identify the availability of information regarding the performance of composites under cryogenic conditions and the use, or not, of suitable measurement standards to obtain this information. Finally, the key requirements and gaps as collected through a workshop with industrial, academic and research colleagues across the UK landscape are presented and key recommendations are summarised.

Hydrogen Fuel and Storage

Hydrogen is a very high energy density element that has great potential to be utilised as fuel. The energy density of hydrogen, which is around 120 MJ/kg, is more than double that of most conventional fuels (see Figure 2). The main issue arises from the fact that hydrogen has very low density. At ambient conditions 1 litre of hydrogen contains only 10.7 kJ of energy. Even in its liquid state the volumetric energy density of hydrogen (8.4 MJ/litre) is less than half that of other fuels, thus storing enough of it for use in most applications requires a large volume. Therefore, to make it practical for mobility applications, the storage method utilized must increase the density of hydrogen.

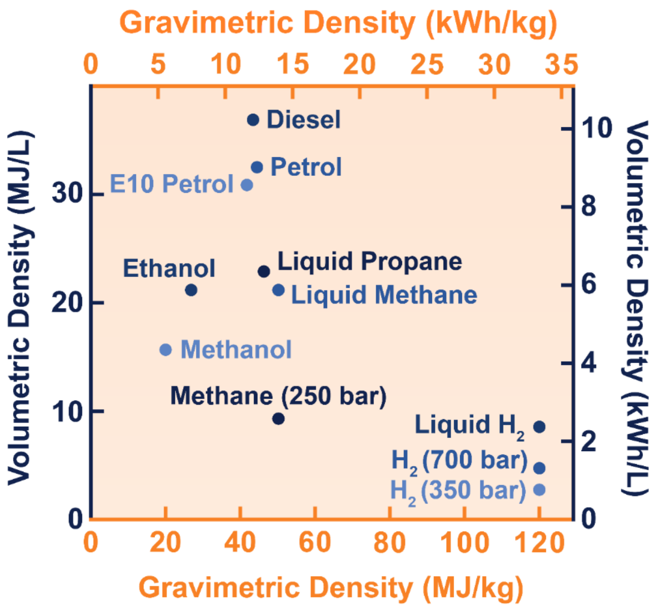

Figure 2. Comparison of specific energy (energy per mass or gravimetric density) and energy density (energy per volume or volumetric density) for several fuels

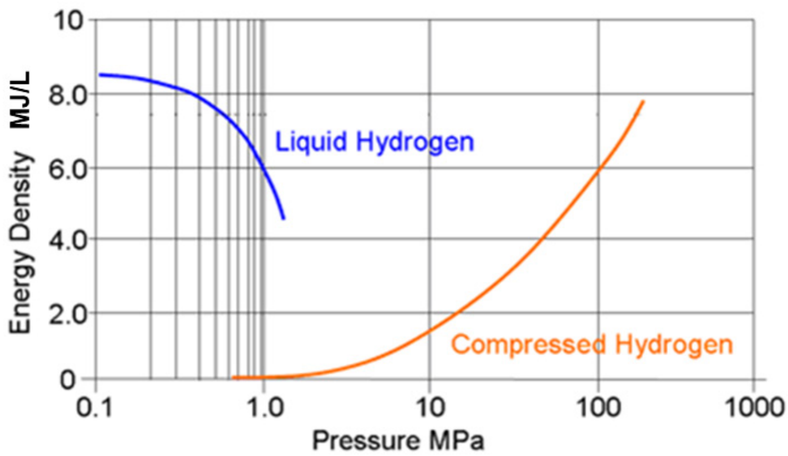

Figure 3. Liquid and gaseous Hydrogen Energy Density vs pressure (from Electrical Power Generation from Hydrogen Fuels [1])

Table 1. Energy densities for various fuels. Data from [2]

Fuel	Ambient state	Gravimetric energy density (MJ/kg)	Liquid state Volumetric energy density (MJ/L)
Hydrogen	Gas	120	8.4 – 10.4[3]
Methane	Gas	50 (43)[2]	21 (17.8)[2]
Ethane	Gas	47.5	23.7
Propane	Gas (liquid)[1]	46.4	22.8
Gasoline	Liquid	44.4	31.1
Ethanol	Liquid	26.8	21.2
Methanol	Liquid	19.9	15.8

[1] A gas at room temperature, but normally stored as a liquid at moderate pressure.
[2] The larger values are for pure methane. The values in parentheses are for a "typical" Natural Gas.
[3] The higher value refers to hydrogen density at the triple point.

Conventional methods of hydrogen storage are as a compressed gas or as a cryogenic liquid. The pressure of compressed gaseous hydrogen needs to increase by two orders of magnitude to achieve the same energy density as liquid hydrogen at moderately low pressures (Figure 3). Cryogenic storage of hydrogen offers the possibility of reducing the tank mass (lower pressure of operation) and volume (higher hydrogen density) compared to high-pressure gas storage. Liquid hydrogen is at a temperature of approximately -253 °C and has a density of 71 kg/m^3, [3]. Thus, cryogenic storage maximizes the density of hydrogen but does impose some significant operational constraints on the storage system:

a. It requires an airtight insulation system to reduce the boil-off of the liquid hydrogen and maintain it at cryogenic temperature,
b. It requires specialized equipment and procedures for handling liquid hydrogen,
c. It introduces a time limitation, due to boil off, to the storage of liquid hydrogen,
d. It requires the storage system to be maintained at a constant pressure, usually around 1.45 bar, to minimize boil-off, which necessitates a venting system and appropriate procedures,
e. It needs the liquid hydrogen tanks and lines to be sealed off from the atmosphere, as air entering the tank will freeze solid and block the flow lines. Only helium can be used as a purge gas.

The main components of a liquid hydrogen system are the tank and insulation. The tank is usually a thin-walled pressure vessel surrounded by a thick layer of insulation. The tank materials must be resistant to hydrogen embrittlement, impermeable to hydrogen gas and capable of structurally withstanding the temperatures of liquid hydrogen. Also, because of the great change in temperature when the tank is filled or emptied, thermal expansion and contraction is a major concern. Because of this it is usually required that the tank be made of one type of material or different materials with similar thermal expansion coefficients. Insulation utilised for the tank as well as any fuel lines or handling devices also need to be designed to reduce the amount of boil-off from the storage tanks and to prevent (or reduce) frost build-up. The insulation must be capable of withstanding the extreme thermal cycling to which it will be subjected. There are two main types of insulation that can be used. The first is a vacuum-jacketed system consisting of layers of low emissivity, high reflectivity materials, surrounded by an outer container capable of maintaining a low pressure within the insulation layers. The vacuum environment minimizes the conductivity between the insulation layers which act as a radiation barrier keeping heat out of the tank. The pressure within the vacuum-jacketed insulation is typically kept at around 0.1 mbar. The main drawback to the vacuum-jacketed insulation is that if the vacuum is lost the insulation will fail. The second type of insulation is a rigid closed-cell foam. This type of insulation can be applied to the outside of the tank. If needed, a thin metal-walled enclosure can be placed on the outside of the foam to maintain its integrity and protect it from damage. The foam type of insulation is much more resistant to catastrophic failure than the vacuum-jacketed type of insulation. However, the density and thermal conductivity of the foam insulation is greater.

Industry drivers

Hydrogen in its liquid form contains about 2.5 times more energy per kilogram than kerosene [4]. When burning, hydrogen only produces water vapor as a by-product, since the fuel has no carbon content to start with. With regards to local air quality, hydrogen combustion produces up to 90% less nitrogen oxides than kerosene fuel, and it eliminates the formation of particulate matter [5].

Hydrogen offers great opportunities but also some limitations for the aviation industry. Burning hydrogen in a jet engine would result in only water vapor emissions. As a fuel it would almost entirely eliminate any carbon-related emissions, including sulphur, particulate matter and nitrogen oxides. However, the architecture of aircraft would have to change considerably to adapt the larger tanks required for hydrogen flight. New aircraft designs would be required (e.g., blended wing body aircraft) potentially resulting in some aerodynamic advantages; however, a downside could be the time involved in certification of radical new aircraft, along with potentially substantial costs to redesign and certify new aircraft and operational infrastructure [6].

The FlyZero [7] project highlighted that in order to achieve a commercially viable, large commercial aircraft, the hydrogen fuel would have to be stored cryogenically as a liquid. Development of the storage tank and fuel distribution system is one of the largest challenges for these aircraft. Some of the technology challenges that would have to be addressed include: (a) achieving a lightweight tank, (b) insulation, to minimise boil-off of hydrogen and the formation of ice, (c) safety, positioning the tank to ensure no chance of rupture in the case of an uncontained engine failure, (d) refuelling, achieving similar refuelling and turnaround times to current aircraft, and (e) materials compatible with hydrogen.

For heavy-duty vehicle applications the requirement is to maximise hydrogen storage while minimising tank weight, volume and cost. The current standard is for 350 bar tanks, either Type 3 or Type 4 and in order to maximise hydrogen storage these tanks are generally large e.g., 2-3 m in length and with an external diameter of at least 400 mm. A recently published report [8] examining various aspects of the use of liquid hydrogen in heavy-duty vehicle applications, especially for fuel-cell transit buses and long-haul trucks, found that storing hydrogen onboard a long haul truck or bus as a cryogenic liquid can increase the range (i.e., miles per refuelling) of the vehicle by a factor of 1.5 to 2 depending on the pressure (350-700 bar) of the hydrogen gas unit being replaced. The report also found that the incremental levelized cost of delivering hydrogen to vehicles can be lower in liquid than in compressed hydrogen stations. However, the H_2 must be liquified at a central liquefaction plant before delivery to the LH_2 station.

2 Regulations and Technical Standards

As part of a product's safety and liability, a manufacturer is obliged to design and manufacture in accordance with the essential health, safety or any other objectives of all product legislation applicable to the product and to carry out the relevant conformity assessment procedure. These obligations are described within the relevant Regulations, Code of Regulations, Directives or Acts developed through national administrative processes or international agreement and occupying the top level of the regulatory hierarchy. Their principal aim is to protect public safety and ensure sustainability.

Codes and technical standards are typically in place to provide specific instructions for technical aspects, addressing the relevant regulation. A code is typically a model, a set of rules that define what needs to be done. Standards support the deployment of legislative acts by providing specific technical guidelines for design, manufacture and testing alongside setting minimum component performance requirements. In effect, standards define how things should be done. Codes and standards are typically voluntary compliance documents and are not legally binding. However, some of the most relevant codes and standards can sometimes be formally referenced in a regulation and thus made legally binding on a similar level as the regulation itself.

In addition, most manufacturers have specific testing requirements that components must successfully pass, based on typical use conditions of the product, and the state of science and technology. The basic hierarchy of a Regulations, Codes and Standards framework for product manufacturing and assurance is shown in Figure 4. A more detailed discussion, including explanation of the role of regulatory authorities and standardisation organisations involved internationally with hydrogen technologies, can be found in [9]

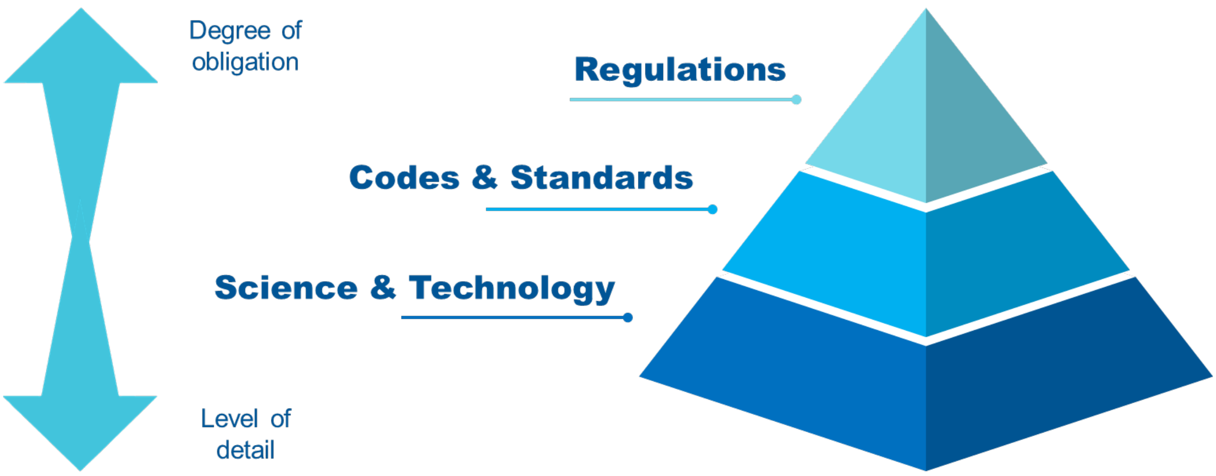

Figure 4. General duties of a manufacturer

Cryogenic Tanks

Cryogenic tanks are an essential part for many industries, as they are a key component to store certain gases crucial for a variety of processes. The structure of cryogenic tanks comprises three main parts:

a. An inner vessel designed to withstand very low temperatures,
b. An outer vessel. In order to guarantee cryogenic temperatures and safety, the inner and outer vessels are insulated from each other by a combination of materials that provide such insulation,
c. In addition to these two containers, a cryogenic storage tank is also equipped with a pressure regulation system, which is specifically designed to ensure that the cryogenic tank always operates at a constant pressure.

While cryogenic tanks have this basic structure in common, it is possible to distinguish between:

a. Vacuum and non-vacuum insulated tanks,
b. Static and transportable tanks.

For vacuum-insulated tanks consisting of two concentric vessels, the interspace between inner and outer vessels is both evacuated and filled with insulating material.

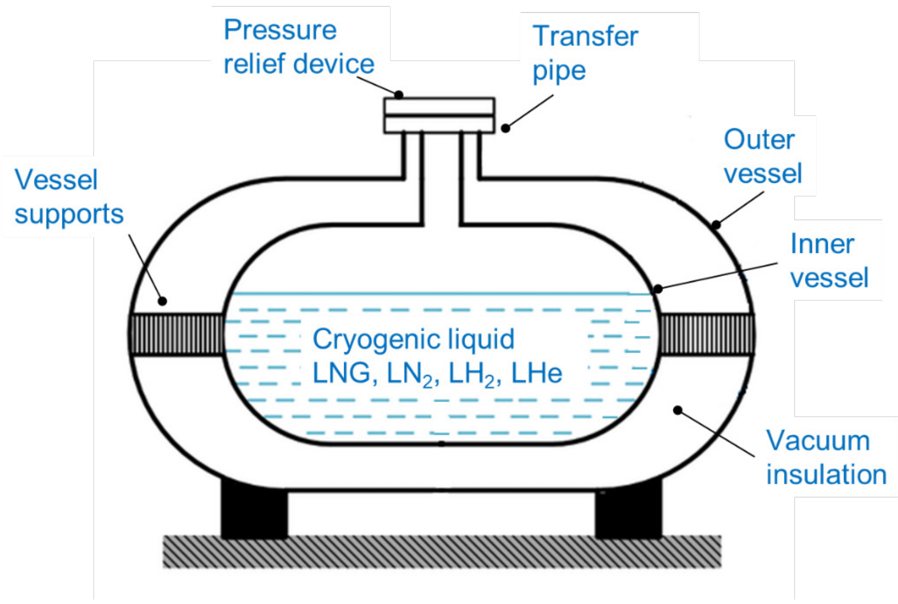

Figure 5. Schematic of a cryogenic liquid tank

Static cryogenic tanks are designed for use in a fixed location. Smaller mobile tanks, mounted on wheels, are also common within workshops and laboratories. Static cryogenic tanks are generally classified as pressure vessels, and as such, new tanks and their associated systems must be manufactured and put into service in accordance with the **Pressure Equipment (Safety) Regulations** [10]**.** Transportable cryogenic tanks that are, or are intended, to be used for the carriage of cryogenic liquids must comply with the **Carriage of Dangerous Goods and Use of Transportable Pressure**

Equipment Regulations [11]. In the EU these are covered by **Directive 2014/68/EU** [12] and **Directive 2010/35/EU** [13]**,** respectively.

At an industry level, the British Compressed Gases Association (BCGA) and the European Industrial Gases Association (EIGA) are enabling organisations to operate safely and grow, by leading safety and technical standards in the storage, transportation, handling and use of industrial, food and medical gases.

At an international level 'ISO/TC 220 – Cryogenic Vessels' is concerned with insulated vessels (vacuum or non-vacuum) for the storage and the transport of refrigerated liquefied gases of class 2 of "Recommendations on the Transport of Dangerous Goods - Model regulations - of the United Nations", and in particular concerning the design of the vessels and their safety accessories, gas/materials compatibility, insulation performance, the operational requirements of the equipment and accessories.

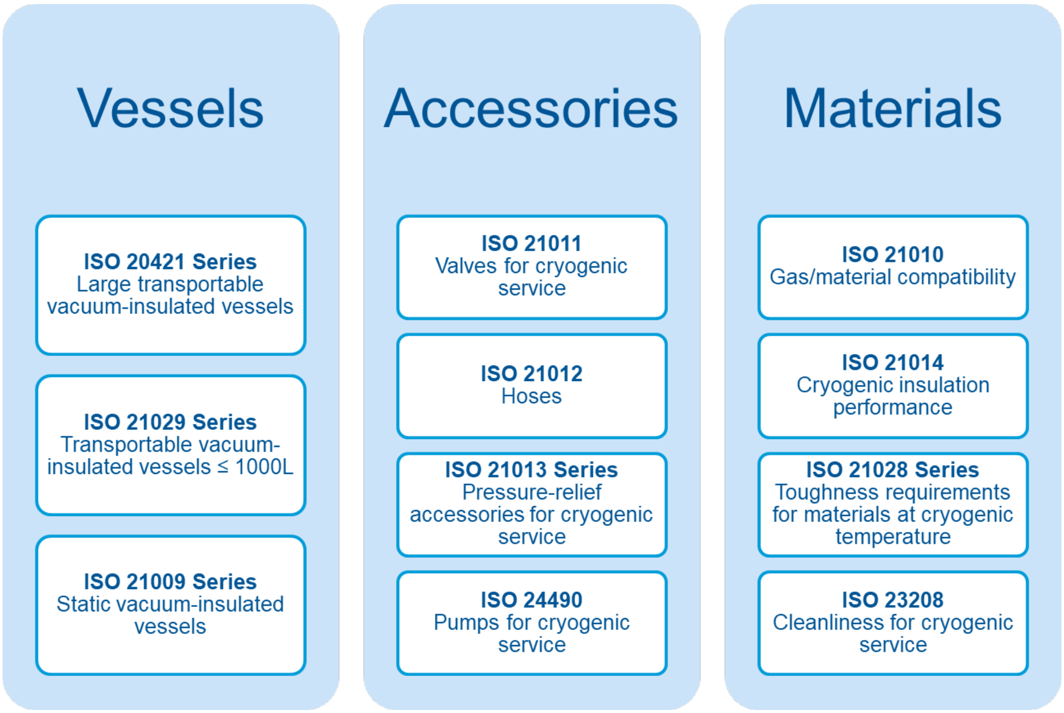

Figure 6. Standards published by ISO/SC 220
(Source: https://www.iso.org/committee/54990/x/catalogue/p/1/u/0/w/0/d/0)

ISO 21010 [14] specifies gas/material compatibility requirements (such as chemical resistance) for cryogenic vessels, but it does not cover mechanical properties (e.g., for low-temperature applications). It provides general guidance for compatibility with gases and detailed compatibility requirements for oxygen and oxygen-enriched atmospheres. For compatibility of materials with gases other than oxygen, the standard refers to ISO 11114-1 [15] (metallic) and ISO 11114-2 [16] (non-metallic), which were produced by 'ISO/TC 58 Gas cylinders', as a guide for cryogenic vessels. However, the scope of ISO 11114-2 specifies that the standard *"is not intended to be used for cryogenic fluids"* and refers back to ISO 21010.

Cryogenic (Hydrogen) Tanks Onboard Vehicle

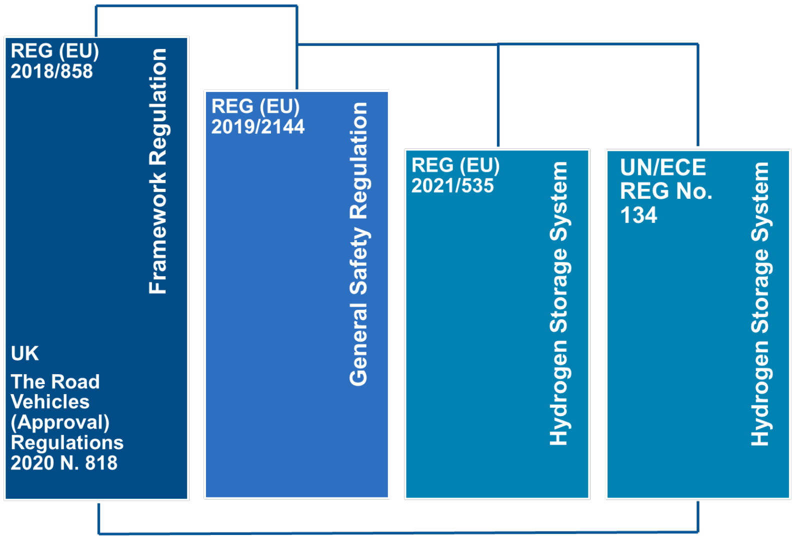

Figure 7. Legal requirements for type-approval of a hydrogen storage system

Regulation (EU) 2018/858 [17] sets out the general framework within the European Union (EU) for the type-approval and market surveillance of vehicles across different classes including passenger cars, buses, trucks, trailers alongside systems and components intended for such vehicles. It lays down the administrative provisions and technical requirements for type-approvals in the EU and is amended by the new **General Safety Regulation (GSR2) (EU) 2019/2144** [18] which focuses on the general road safety and the protection of vehicle occupants and vulnerable road users. Furthermore, implementing **Regulation (EU) 2021/535**, lays down rules for the application of GSR2. It is based on a safety-related regulation for vehicles of categories M, N and O and hydrogen systems and components designed for those types of vehicles and also provides for uniform procedures allowing European type-approval. For hydrogen-powered vehicles, this regulation mentions the safety performance and material compatibility of Liquid Hydrogen Storage System (LHSS) and Compressed Hydrogen Storage System (CHSS) in Annex XIV. Alongside this Regulation, to receive type-approval vehicles must comply with several separate technical Directives, such as **UN/ECE Regulation No. 134** [19]. Because of the narrow scope of these regulations and withdrawal of others [20], a number of components critical for a hydrogen-powered vehicle will be left with no applicable type-approval framework, as they simply are not within the scope of UN/ECE Regulation No. 134 and Regulation (EU) 2021/535. The scale of the issue including liquid hydrogen storage is comprehensively presented in [20].

In the UK the **Road Vehicles (Approval) Regulations** [21] set the regulation framework for type-approval.

At international standards level, 'ISO/TC 197 Hydrogen technologies' has published ISO 13985 [22] that specifies the construction requirements for refillable fuel tanks for liquid hydrogen used in land vehicles as well as the testing methods required to ensure that a reasonable level of protection from loss of life and property resulting from fire and explosion is provided. It is applicable to fuel tanks intended to be permanently attached to land vehicles of categories M1-3 and N1-3 (see Figure 9). The standard allows for the use of non-metallic materials providing *"low temperature suitability shall be validated by an experimental method, taking into account the service conditions"*. However, all cross-referenced standards for design, manufacture and testing refer to metallic vessels.

'ISO/TC 8 Ships and Marine Technology' is another technical committee active in this field and currently working on an item that is intended to specify the test procedures and requirements for the performance tests that shall be conducted in order to confirm the mechanical features of the hydrogen storage tank.

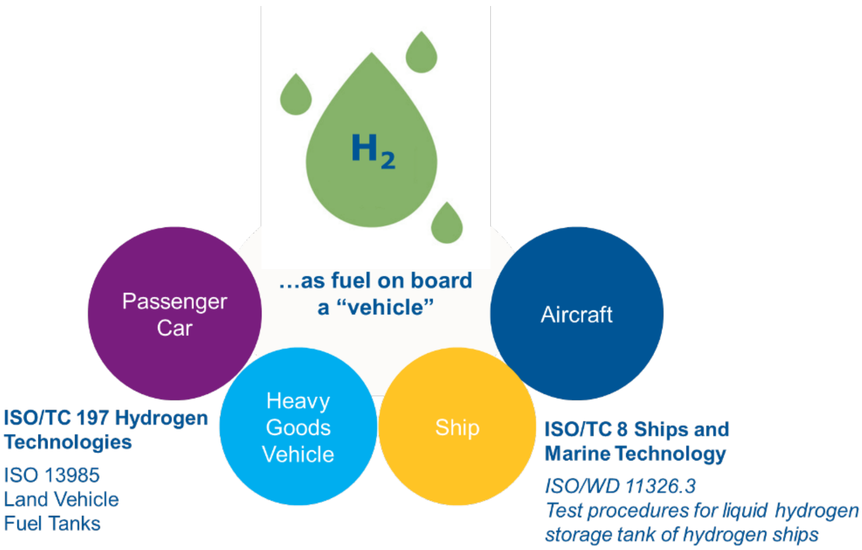

Figure 8. Standards for hydrogen storage as fuel onboard a vehicle

L	Motor cycle	
M1	Passenger vehicle	
M2,M3	Bus	
N1	Light duty truck	
N2, N3	Heavy duty truck	
O	Trailer	

Figure 9. Vehicle categories

3 Materials and Measurement Standards for Cryogenic Temperatures

Polymers and composites have been developed and used since the 1970s in cryogenic applications such as insulation of superconducting magnets, as well as spacecraft and launch vehicle applications [23]. However, it is only until fairly recently that they have been identified as potential materials for the manufacture of liquid hydrogen tanks for sustainable aerospace applications [7, 24]. Unlike composites, metallic materials have been extensively used for cryogenic applications, and the associated research and development has been widely reported and standardised since the early 2000s [25].

The information presented in this section has been collated from an extensive literature review of more than 150 relevant sources of information published over the last 30 years or so. The aim was to provide a brief overview of the materials, properties, and measurement methods that have been researched over this period. The majority of the mechanical test standards for fibre-reinforced composites date back to the mid-90s onwards; as a result, most of the publications reviewed for this study were published following that period.

The literature review revealed a high level of variability across material properties data [23, 26, 27, 28, 29, 30], which is thought to be due to the lack of standards providing guidance [23, 26] on mechanical testing of FRP composites at cryogenic temperatures, including details for apparatus for such tests, instrumentation, preparation, etc. The charts in Figure 10 present the proportion (to the total number of literature sources reviewed), of: (a) material types, (b) temperature range, (c) material properties, and; (d) measurement standards used and openly reported.

It is evident that the most researched composite material types are carbon and glass fibre-reinforced thermosets, with thermoplastics receiving significantly less attention (Figure 10a). This can be attributed to their well-established manufacturing processes and extensively reported properties across a range of applications.

Table 2. Commonly used cryogenic fluids and boiling points.

Fluid	Boiling point	
	°C	K
Liquefied Natural Gas (LNG)	-162	111.15
Liquid Oxygen (LOx)	-183	90.15
Liquid Nitrogen (LN_2)	-195.8	77.35
Liquid Hydrogen (LH_2)	-252.8	20.35
Liquid Helium (LHe)	-268.9	4.25

The field of cryogenics is defined as relating to temperatures below -150 °C, where the boiling points of gases such as natural gas (LNG), oxygen (LOx), nitrogen (LN_2), hydrogen (LH_2), and helium (LHe) occur, see Table 2. The researched literature sources reported primarily test results at cryogenic temperatures over the range of 25 to 77 K (Figure 10 b). This shows a significant interest for cryogenic applications around the boiling points of LN_2 and LH_2.

Figure 10 c presents the types of measured properties, as reported in the literature, for composite materials at cryogenic temperatures. Mechanical tests such as tension, flexure, fracture toughness, impact and compression have been researched. Also covered are thermal properties, such as the coefficient of thermal expansion and thermal conductivity as well as permeability characteristics. In addition to the variability in the response of mechanical properties at cryogenic temperatures, some authors have observed more complex behaviour with a decrease in temperature, such as matrix micro and macro-cracking [26, 30].

An overview of the test standards used when testing at cryogenic temperatures is presented in Figure 10 d. The majority of publications reported not having followed any specific standard, which highlights the lack of universal testing methods that provide guidance for such tests. Specifically for tension, which is the dominant property researched, the test methods used, refer to pre-existing test standards, created initially for ambient temperature property characterisation. There was no evidence that existing standards developed for metallic materials (summarised in [31]), have been adopted and modified.

The lack of standards for mechanical testing of FRP composite materials at cryogenic temperatures can be considered a barrier to the uptake of new materials and processes in cryogenic applications.

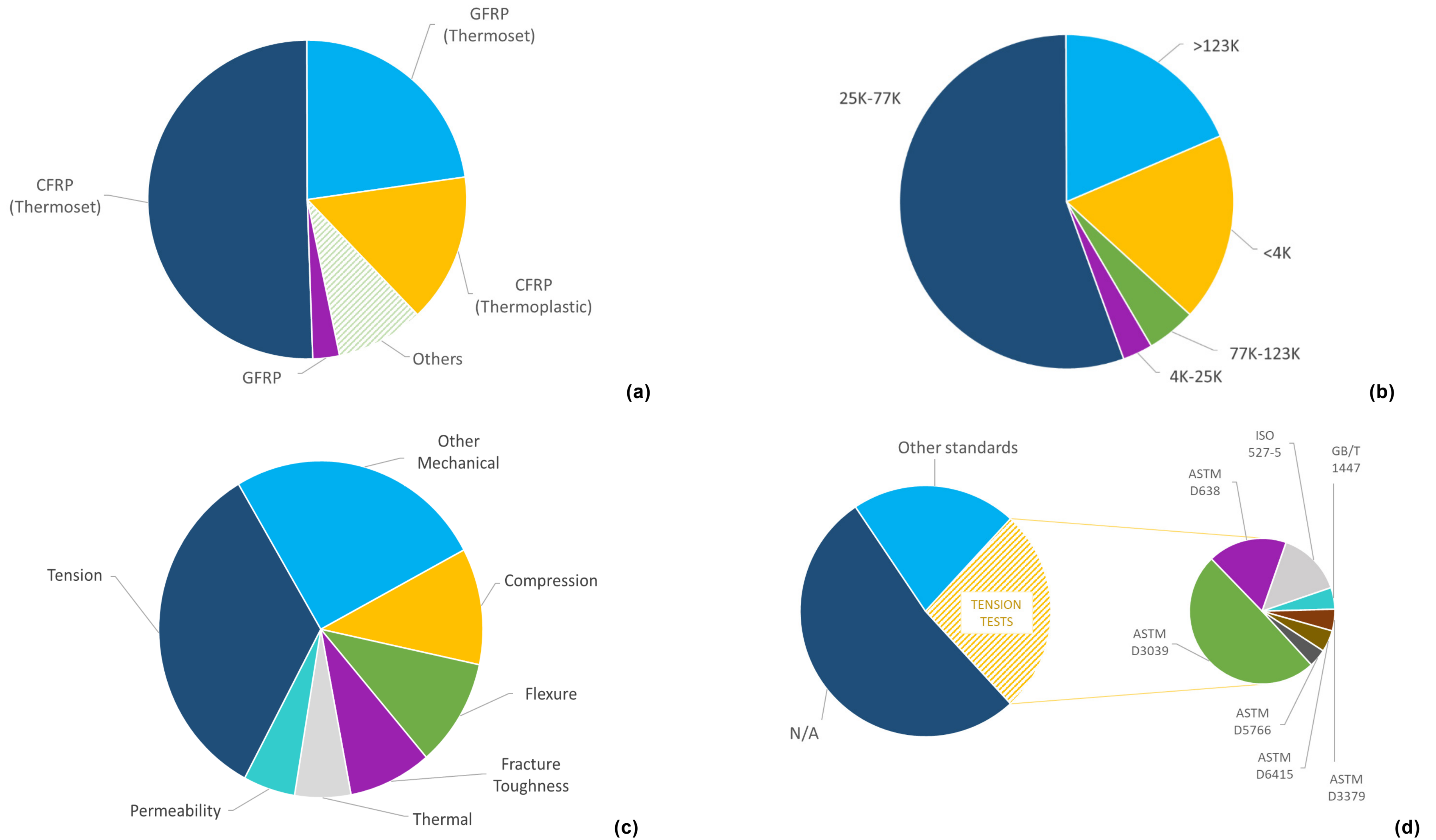

Figure 10. Distribution of reported polymer composites research over the last 30-years per (a) material type, (b) temperature range, (c) material properties and (d) measurement standards

4 Cryogenic Materials, Properties & Standards Workshop

On September 29th, 2022, the National Physical Laboratory (NPL) held a half-day virtual workshop focused on cryogenic materials, properties and standards. The main workshop objectives were:

1. Identify gaps in (design) codes & standards that prevent the qualification and subsequent use of advanced materials in cryogenic applications,
2. Identify key material properties that need to be measured at cryogenic conditions and potential gaps in measurement infrastructure,
3. Prioritise (highest impact and/or quickest wins) the identified points and draw recommendations for next steps,
4. Capture current best practice and disseminate via appropriate channels.

In total, 27 attendees (excluding 5 NPL staff) participated in the workshop, with presentations and an open forum discussion.

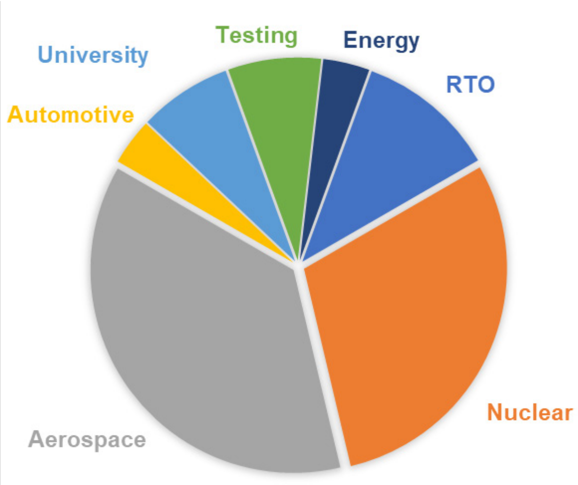

Figure 11. Workshop attendees

The attendees represented the interests and requirements from across a number of industry sectors (Aerospace, Nuclear, Automotive and Energy) as well as Research & Technology Organisations (RTOs) and Universities.

NPL would like to thank the external speakers who presented at the virtual workshop, James Minshull (Aerospace Technology Institute) and Wendel Bailey (University of Southampton).

A presentation by NPL set the scene of the workshop by using Liquid Hydrogen Storage as the use case for the increasing need to understand materials performance at cryogenic environments and the associated technical standards. The open forum discussion was organised over two sessions, the first on Regulations, Codes and Standards and the second on Testing Capabilities and guided by four key questions:

Q1: What are the regulatory requirements for materials, structures & products operating at cryogenic temperatures (< 100K)?
Q2: What are the gaps in test standards & procedures preventing the qualification of materials at cryogenic temperatures?
Q3: What cryogenic related properties are key and need to be measured via validated tests procedures?
Q4: What common good practice in cryogenic testing can be shared more widely?

The key outcomes of the productive discussions can be summarised as follows:

Regulations, design codes & technical standards

Regulations: There is a need for signposting as well as revising existing regulations that address all the safety factors during the whole operating life of products that involve cryogenic liquids e.g., fuel tanks onboard an aircraft.

Technical standards: There is an extensive set of pressure vessel and cryogenic container design codes (see Section 2), but the majority are concerned with metallic materials, associated manufacturing processes and validation testing. These would need to be extended to cover other advanced engineering materials (e.g., polymer matrix composites) to allow for the introduction of further innovative products to the market. Since the workshop, participating countries in ISO/TC 197 voted for a revision and expansion of scope for ISO 13985 *Liquid hydrogen — Land vehicle fuel tanks*.

It was also suggested that to unlock product development and paths to certification, product specific requirements (e.g., for a cryogenic fuel tank) will need to be created. These will aim to relate the design approach to the necessary low-level materials performance (highest risk / priority) test requirements. In addition, for the case of polymer composite products there is a need to create technical guidance for testing at component level (rather than materials level) for properties that are particularly sensitive to manufacturing processes and exploitation of validated virtual testing that will pave the way for digital certification.

Testing infrastructure

Another key discussion point was the practical challenges associated with testing material at cryogenic temperatures as low as 4K. Some of the key points for consideration moving forward are as follows:

Temperature: Current temperature measurement verification approaches would need to be reviewed for cryogenic test conditions, and potentially an approach like the test system verification described in the ISO/TS 21913:2022 *Temperature verification method applied to dynamic fatigue testing* might have to be introduced.

Strain: Errors and uncertainty in extensometers or other methods for strain measurement need be reviewed, as most of the systems might be rated down to 4K but primarily designed to be operated in air rather than a turbulent fluid e.g., liquid nitrogen and/or helium.

Jigs and fittings: The suitability of jigs and fittings prescribed in existing mechanical measurement standard test procedures would need to be reviewed for testing at cryogenic temperatures, and in cases of fully immersion in cryogenic liquids.

Cryogenic system: Alternative to liquid nitrogen and/or helium systems, such as cryocoolers, would need to be investigated. Typical cryogenic liquid full immersion test setups might require slow loading rates to ensure that the working liquid remains still which might be an issue for long-term fatigue testing.

Key properties and test procedures

During the discussion sessions several key material properties were identified based on design requirements for different applications across the industry sectors. These are summarized in Table 3.

Table 3. Needs for cryogenic material (metallic and non-metallic) properties and testing procedures

Mechanical	Thermal	Physical	Damage characteristics
Tension, compression, and fracture toughness under static loading Low and high cycle fatigue with damage accumulation and growth	Thermal expansion and thermal conductivity Thermal fatigue including thermal shock and thermal gradients	Mass transport properties including diffusion and permeation Low temperature superconductivity properties including critical temperature, irreversibility line and critical current density	*For composites*, intralaminar matrix cracking and fibre interfacial dis-bonding driven by thermal shock/gradients *For metallic materials*, embrittlement including micro-cracking initiation and propagation

Knowledge transfer and collaboration

Finally, the participants discussed ways that existing and new knowledge could be disseminated to interested parties in the community. There was high level of agreement on the following keys points:

- The establishment of an **Advisory Group** to bring the community together would be extremely beneficial. This group could act as the springboard for the set-up of a future Joint Industry Project (JIP) to tackle generic cryogenic measurement issues across industries and applications.
- **Knowledge transfer** from existing standards and good practices to other materials and industries is of paramount importance. For example, using *ISO 6892-4:2015 Metallic materials — Tensile testing — Part 4: Method of test in liquid helium* as the basis, transfer knowledge to composite materials.
- Simple **guidance documents** (*CryoFacts*) to disseminate existing and new knowledge on measurement methods could be generated and publicly disseminated via the advisory group.

- There needs to be encouragement for the **open sharing of validated and trusted data** to minimize duplication and enable short term wins in new ambitious designs.

5 Summary

This study focuses in identifying possible barriers in realising liquid hydrogen cryogenic storage, particularly when utilising lightweight polymer composite materials essential for some applications like on-board vehicle storage. Some of the key findings are as follows:

Regulations and technical standards

- Existing regulations on pressure equipment safety and carriage of dangerous goods and use of transportable pressure equipment, provide the legal framework for large scale cryogenic liquid storage,
- The available technical standards developed via 'ISO/TC 220 Cryogenic vessels' and 'ISO/TC 58 Gas cylinders' committees provide a satisfactory framework, though they are prescriptive and at present allow mainly for metallic materials to be utilised in the body of the storage container,
- For storage of liquid hydrogen as fuel on-board a vehicle, there is a gap left at the top of the regulatory framework with the recent repealing of Regulation (EC) 79/2009 and the narrower scope of UN/ECE Regulation No. 134 and a number of components critical for a hydrogen-powered vehicle were left with no applicable type-approval framework,
- The 'ISO/TC 197 Hydrogen technologies' committee has published a technical standard that specifies the construction requirements for refillable fuel tanks for liquid hydrogen used in land vehicles as well as the testing methods required to ensure that a reasonable level of protection from loss of life and property resulting from fire and explosion is provided. The standard allows for the use of non-metallic materials, however further improvements are required for this to be realised.

Materials and measurement standards

- There is a significant body of primarily academic literature referring to cryogenic performance of composite materials over the last 30 years covering thermoset and thermoplastic FRP composites, over a temperature range as low as 4K and including properties such as mechanical (tension, compression, flexure, fracture toughness etc.), thermal (thermal expansion, thermal conductivity) and physical (permeability characteristics).
- The reported material properties show a high level of variability which can be largely attributed to the lack of validated measurement methods for composites at cryogenic temperatures.
- Significant gaps exist in the measurement infrastructure, with temperature verification approaches, uncertainty of strain measurement systems as well as

suitability of existing jigs and fittings being key for realising validated and trusted material properties data.

- Discussions with several industry, academia and research stakeholders suggested that an Advisory Group to bring the community together would be extremely beneficial and can act as the springboard for the set-up of a future project to tackle generic cryogenic measurement issues across industries and applications.

6 References

[1] "https://www.mpoweruk.com/hydrogen_fuel.htm," [Online]. [Accessed December 2022].

[2] G. Thomas, "Overview of Storage Development DOE Hydrogen Program: Annual Review," US DOE, San Ramon, CA, May 2000.

[3] " https://www1.eere.energy.gov/hydrogenandfuelcells/tech_validation/pdfs/fcm01r0.pdf," [Online]. [Accessed October 2022].

[4] Y. Najjar, "Hydrogen safety: The road toward green technology," *Journal of Hydrogen Energy ,* vol. 38, pp. 10716-10728, 2013.

[5] P. Agarwal, X. Sun, P. Gauthier and V. Sethi, "Injector design space exploration for an ultra-low NOx Hydrogen micromix combustion system GT2019-90833," *Proceedings of ASME Turbo Expo 2019, Phoenix Arizona.,* vol. 38, 2019.

[6] "Liquid hydrogen asa potential low-carbon fuel for aviation," *IATA Fact Sheet 7,* August 2019.

[7] Aerospace Technology Institute, "FlyZero Advanced Materials: A Key Enabler for Zero-Carbon Emission Commercial Flight," March 2022.

[8] A. Burke and L. Fulton, "Use Of Liquid Hydrogen in Heavy-Duty Vehicle Applications: Station And Vehicle Technology and Cost Considerations," UC Davis Institute of Transportation Studies, 2022.

[9] A. Tchouvelev, S. De Oliveira and N. Neves, "Science and Engineering of Hydrogen-Based Energy Technologies: Hydrogen Production and Practical Applications in Energy Generation," in *Regulatory Framework, Safety Aspects and Social Acceptance of Hydrogen Energy Technologies.*, P.E. Academic Press, 2018, pp. 303-356.

[10] Legislation.co.uk, "The Pressure Systems Safety Regulations 2016 No.1105," [Online]. Available: https://www.legislation.gov.uk/uksi/2016/1105/contents.

[11] Legislation.co.uk, "The Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations 2009 No. 1348," [Online]. Available: https://www.legislation.gov.uk/uksi/2009/1348/contents/made.

[12] European Union, "European Commission. Directive 2014/68/EU on the harmonisation of the laws of the Member States relating to the making available on the market of pressure equipment.," Official Journal of the European Union, L 189/164, 2014.

[13] European Commission, "Directive 2010/35/EU on transportable pressure equipment and repealing Council Directives 76/767/EEC, 84/525/EEC, 84/526/EEC, 84/527/EEC and 1999/36/EC.," Official Journal of the European Union, L 165/1, 2010.

[14] *ISO 21010:2017 Cryogenic vessels — Gas/material compatibility.*

[15] *ISO 11114-1:2020 Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic materials.*

[16] *ISO 11114-2:2021 Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials.*

[17] European Comission, "Regulation (EU) 2018/858 on the approval and market surveillance of motor vehicles and their trailers, and of systems, components and separate technical units intended for such vehicles," amending Regulations (EC) No 715/2007, 595/2009 and repealing Directive 2007/46/EC. Official Journal of the European Union L 151/1, 2018.

[18] European Comission, "Regulation (EU) 2019/2144 on type-approval requirements for motor vehicles and their trailers, and systems, components and separate technical units intended for such vehicles, as regards their general safety and the protection of vehicle occupants," Journal of the European Union, L 325/1, 2019.

[19] Economic Commission for Europe of the United Nations (UN/ECE), "Regulation No 134 of UN/ECE – Uniform provisions concerning the approval of motor vehicles and their components with regard to safety-related performance of hydrogen-fuelled vehicles (HFVC).," Official Journal of the European Union, L 129/43, 2019.

[20] M. Sekura and T. Frohn, "EU type approval of hydrogen-powered vehicles and their components after repeal of Regulation (EC) 79/2009.," TÜV, 2022.

[21] Legislation.co.uk, "The Road Vehicles (Approval) Regulations 2020 No. 818," [Online]. Available: https://www.legislation.gov.uk/uksi/2020/818/contents.

[22] *ISO 13985:2006 Liquid hydrogen — Land vehicle fuel tanks.*

[23] R. P. Reed and M. Golda, "Cryogenic properties of unidirectional composites," *Cryogenics,* vol. 34, no. 11, 1994.

[24] Clean Sky 2, "Hydrogen-powered aviation: A fact-based study of hydrogen technology, economics and climate impact by 2050.," May 2020.

[25] National Aeronautics and Space Administration, "Properties of cryogenically worked metals," 1975.

[26] Z. Sápi and R. Butler, Properties of cryogenic and low temperature composite materials – A review, 2020.

[27] D. Chen, J. Li, Y. Yuan, C. Gao, Y. Cui, S. Li, X. Liu and H. Wang, “A Review of the Polymer for Cryogenic Application: Methods, Mechanisms and Perspectives,,” 2021.

[28] M. Kim, S. Kang, C. Kim and C. Kong, ““Tensile Properties of Carbon Fiber Composites with Different Resin Compositions at Cryogenic Temperatures,”,” *Advanced Composite Materials.,* 2010.

[29] R. Reed, M. Madhukar, B. Thaicharoenporn and N. Martovetsky, “Low-temperature mechanical properties of glass/epoxy laminates,,” *Advances in Cryogenic Engineering,* 2014.

[30] J. Hohe, A. Neubrand, S. Fliegener, C. Beckman, M. Schober, K.-P. Weiss and S. Appel, “Performance of fiber reinforced materials under cryogenic conditions—A review,” *Composites Part A,* vol. 141, 2022.

[31] N. Salmeron Perez, R. Shaw and M. Gower, “Mechanical Testing of Fibre-Reinforced Polymer Matrix Composites at Cryogenic Temperatures: Requirements for Mechanical Test Capability at - 269°C (4 K),” NPL Report MAT 102, 2022.