INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–8

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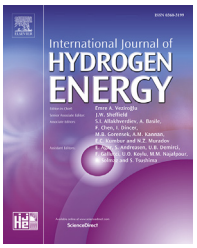

Polymer coated glass capillaries and structures for high-pressure hydrogen storage: Permeability and hydrogen tightness

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ARTICLE INFO

Article history:
Received 12 June 2017
Received in revised form
23 November 2017
Accepted 16 December 2017
Available online xxx

Keywords:
Permeability
Glass capillaries
Coating
Hydrogen storage
Long-term calculation
Epoxy resin

ABSTRACT

The hydrogen tightness of high-pressure hydrogen storage is a basic criterion for long-term storage. The H_2 permeation coefficients of epoxy resin and a glass lacquer were determined to enable the geometric optimization of a glass capillary storage. It was found that the curing conditions have no significant influence on the H_2 permeation coefficient of resin. The H_2 permeation coefficient of epoxy resin is only about three orders of magnitude greater than that of borosilicate glass. This suggests that the initial pressure of 700 bar takes about 2.5 years to be halved in capillary array storage. Therefore, a high-pressure hydrogen storage tank based on glass capillaries is ideally suited for long-term storage in mobile applications.

Introduction

Energy storage is a key issue in the field of renewable energy. Hydrogen would be an ideal energy storage medium since it can be produced without greenhouse gas emissions. In addition, its gravimetric energy density is 33.3 $\frac{kWh}{kg}$ which is a factor of 3 greater than that of gasoline and even a factor of 7 greater than that of coal [1–3]. A key problem is that lightweight, cost-efficient and safe solutions are necessary to store H_2 with sufficient volumetric density to enable mobile applications to be implemented [1,4,5]. Current technologies for hydrogen storage are liquid storages, metal-organic frameworks, chemical storages, metal hydrides, pressure storages in composites tanks or glass microspheres [6]. The volumetric capacity varied between 30 and 115 $\frac{g}{l}$ and the gravimetric density between 6 and 17 wt% depending on the technology [6–9]. A new approach is storing hydrogen in micro glass capillaries [10] or capillary arrays under high pressure up to 700 bar within a temperature range of between −40 °C and 60 °C [11,12]. Advantages are controlled loading and unloading, superior mechanical strength of pristine micro glass components, low density and no creep or plastic flow even for long-term stress conditions. In addition, glass is an exceptionally efficient barrier against hydrogen that allows the long-term H_2 storage [11,13]. In order to take advantage of the

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https://doi.org/10.1016/j.ijhydene.2017.12.092

superior mechanical properties of pristine micro glass containers their surface has to be protected from mechanical damages, e.g. by coating with polymers or glass lacquers. To utilize the benefit of the efficient barrier properties of glass allowing long-term storage, adhesive bonds between the class capillary and its sealing cap (e.g. epoxy resin) must also have a sufficient barrier effect. Consequently, the permeation properties of polymers used must be understood. However, there is little information available in the literature. In the present paper the permeability of epoxy resin and glass lacquer is determined. The data determined experimentally were used to calculate the pressure loss of the storage for varies storage modules and geometries and conclusions were drawn for component optimization.

Materials and methods

Materials

Hydrogen permeation was measured on a glass lacquer from Plantag Coatings GmbH (acrylate-polycarbonate-PU-dispersion) and the epoxy resin Hysol 9483 from Loctite. The curing temperature of resin was varied: $T_1 = 25^\circ C$, $T_2 = 50^\circ C$ and $T_3 = 100^\circ C$.

Permeation

Hydrogen permeability, P_{H_2}, of epoxy resin and glass lacquer was measured with the cylinder method, that belongs to the transmission or leak rate methods. For this sake, cylinders of epoxy resin (inner diameter $D_i = 9\ mm$, length $l = 35\ mm$, wall thickness $d = 0.4\ mm$) were made (Fig. 1, blue cylinder). The Teflon casting moulds were filled with the epoxy resin and cured at $T_1 = 25^\circ C$, $T_2 = 50^\circ C$ and $3 = 100^\circ C$ for 24 h, 10 h and 10 h. After curing, the inner diameter is drilled. The outer diameter is realized with turning of the lathe. The feed ($1.5 bar H_2$) and permeate (mass spectrometer MS) sides were separated vacuum-tight from each other by the test sample. The feed side was separated with a glass tube from the environment. Both sides were evacuated prior to the experiment. The feed side was additionally purged with hydrogen. After reaching sufficiently low pressure $p_{MS} \leq 1 \cdot 10^{-6} mbar$ on the permeate side, the feed side was loaded with a constant pressure of $p_{H_2} = 1.5 bar$. The resulting gas flow was analyzed by MS. In this case, the ion current I_{H_2} of $\frac{m}{e} = 2$ was analyzed, that is a measure for the partial pressure p_{H_2} of the permeated H_2 according to: Eq. (1).

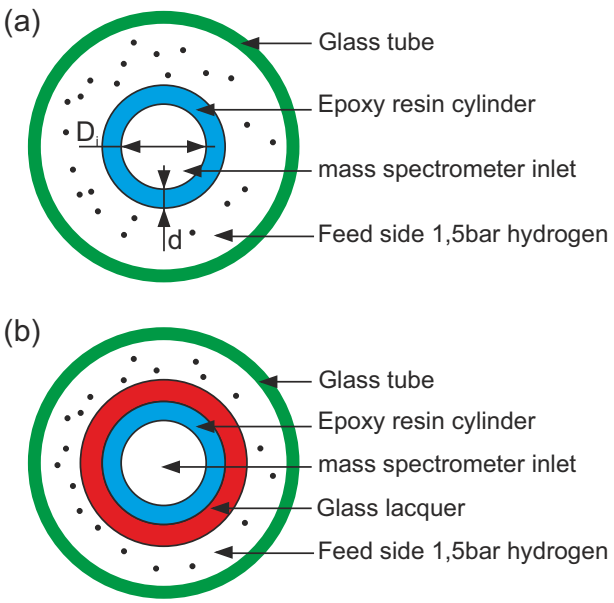

Fig. 1 – Schematic representation of permeation measurement with mono-layer (a) and multi-layer (b) setup.

$$p_{H_2} \sim I_{H_2} \tag{1}$$

Consequently, I_{H_2} corresponds to a permeation rate $\frac{dQ}{dt}$ according to: Eq. (2), where K is a calibration factor.

$$\frac{dQ}{dt} = K \cdot I_{H_2} \tag{2}$$

The permeability, P, for H_2 of the epoxy resin can be calculated as Eq. (3), where K is an calibration factor, $\frac{dQ}{dt}$ the permeation rate, d the wall thickness (d is an average of five measurements), A the surface from specimen and Δp the pressure difference.

$$P = \frac{dQ}{dt}\frac{d}{\Delta p A} \tag{3}$$

P measured at different temperatures can be illustrated in an Arrhenius diagram. The slope (Eq. (4)) in this diagram corresponds to the activation energy, E_P, of the permeation process.

$$P = P_0 \exp\left[-\frac{E_P}{RT}\right] \tag{4}$$

Multi layer method

The multi-layer model (Fig. 1) had to be used to test glass lacquer since no test sample of sufficient mechanical stability was available. The ideal laminate model (Eq. (5)) was used for the evaluation, where P_i is the permeation coefficient of the individual layers and d_i is their thickness.

$$\frac{d_{tot}}{P_{tot}} = \sum_{i=1}^{n} \frac{d_i}{P_i} \tag{5}$$

This model assumes that all cylinder layers are defect-free and perfectly adhere to each other. In the present case, the composite consisted of two layers (i = 2). In order to measure the H_2 permeability P for glass lacquer, a reference body made of epoxy resin was first tested for its permeation. Subsequently, a specified layer thickness of glass lacquer was applied to the reference body using an airbrush and the permeation measurement was repeated. Since the thicknesses of the individual layers and the permeation properties of both the reference body and the coated body were known, permeability of glass lacquer could be calculated by Eq. (6).

$$P_1 = \frac{d_1}{\frac{d_{tot}}{P_{tot}} - \frac{d_2}{P_2}} \tag{6}$$

Please cite this article in press as: Prewitz M, et al., Polymer coated glass capillaries and structures for high-pressure hydrogen storage: Permeability and hydrogen tightness, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.092