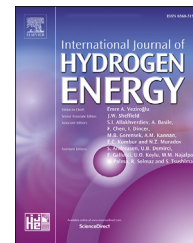




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Evaluation of hydrogen sorption and permeation parameters in liquid metal membranes via Sieverts' apparatus

Nicholas D. Deveau, Pei-Shan Yen, Ravindra Datta*

Fuel Cell Center, Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Rd, Worcester, MA 01609, USA

ARTICLE INFO

Article history:

Received 16 June 2018

Received in revised form

14 August 2018

Accepted 17 August 2018

Available online 12 September 2018

Keywords:

Sieverts' apparatus

Metal-hydrogen system

Liquid metal

Hydrogen sorption

Hydrogen diffusion

ABSTRACT

We have recently proposed sandwiched liquid metal membranes (SLiMM) for hydrogen separation. To evaluate SLiMM, thermodynamic and kinetic parameters such as the solubility, diffusion coefficient, and absorption kinetics of hydrogen in the liquid metal are needed. While there are some theoretical approaches to estimate these parameters, including our own published recently, it is important to obtain experimental corroboration. This study utilizes the classical Sieverts' apparatus in an effort to estimate these parameters by monitoring the change in pressure with time of hydrogen introduced over a pool of liquid metal within a container. The solubility was calculated from the change in pressure over the entire duration of the experiment as it attained equilibrium, while typically the diffusion coefficient could be determined from the short-time response. The theory behind the Sieverts' apparatus is extended here to provide full-time solution by linearizing Sieverts' law, along with early (very short) time solutions to determine the sorption kinetics in addition to the diffusion coefficient. In this manner, new theoretical and experimental results are obtained for hydrogen sorption and diffusion in liquid gallium and indium at different temperatures. The results corroborate the hydrogen permeability in a gallium SLiMM.

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Introduction

Due to the increasing demand for pure hydrogen in applications at different scales ranging from chemicals to fuel cells, there is significant interest in developing dense metal membranes for separation and purification of hydrogen. These metal membranes promise to be more energy efficient and selective when compared to traditional hydrogen purification technologies such as pressure swing adsorption [1]. The state-

of-the-art dense metal membrane for hydrogen uses palladium or its alloys with silver and copper, manufactured as thin foils or as thin but dense membranes deposited on a porous support. While very promising, these membranes have some distinct disadvantages. Palladium, and to a lesser extent silver, is expensive. These membranes also come up short in regard to durability, as exceedingly thin membranes (~10–20 μm) are employed to concomitantly reduce cost and increase permeance. Further, these solid but thin films can develop cracks and micropores that allow other gases to pass

* Corresponding author.

E-mail address: rdatta@wpi.edu (R. Datta).

<https://doi.org/10.1016/j.ijhydene.2018.08.101>

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through and hence reduce membrane selectivity and product purity. Such defects cannot easily be repaired, requiring membrane replacement.

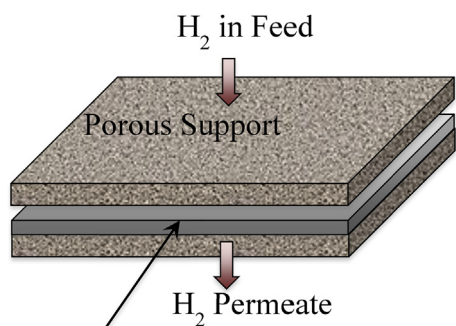
These limitations are driving research into seeking alternative and cheaper metals with adequate hydrogen permeability [2–9], which could be fashioned into thicker, more robust, solid membranes. In this vein, we have for the first time recently proposed thicker films (~200 μm) of low-melting metals or alloys as sandwiched liquid metal membranes (SLiMMs), as shown schematically in Fig. 1 [10]. Such liquid metal membranes could potentially address some of the issues associated with solid metal membranes, e.g., sintering, hydrogen embrittlement, and thermal mismatch between support and membrane. However, liquid metals provide their own challenges. There is limited literature on liquid metal membranes due to their high reactivity with other metals [11–16], as well as wettability issues [17] with ceramic supports. There is limited data on the formation of hydrides with liquid metals and any molecular species diffusion. Although there is limited available experimental results, they indicate that the solubility and diffusivity of hydrogen of a metal increases upon melting [10]. Here, we utilize Sieverts' apparatus to determine the relevant parameters for two low melting metals of interest for SLiMM, namely, gallium (29.8 °C, MP) and indium (156.6 °C, MP), and compare these to our recent theoretical predictions [18].

The hydrogen permeation in a metal, as proposed by Wang and Roberts [19], consists of five sequential steps, described schematically in Fig. 2. Thus, hydrogen is first dissociatively adsorbed onto the metal surface on the feed side, and then penetrates to the sub-surface of the bulk metal. Next, the hydrogen atoms interstitially diffuse across the membrane, ultimately emerging on the opposite surface. The final step is the associative desorption of hydrogen from the second surface of the metal membrane on the permeate side.

The flux of hydrogen (N_{H_2}) in traditional palladium-based membranes is described using what is commonly known as Sieverts' law [20], first proposed by Richardson et al. [21],

$$N_{\text{H}_2} = \left(\frac{c_t \chi_{\text{H-M}} K_S D_{\text{H}}}{2\delta \sqrt{p^0}} \right) (p_{\text{H}_2, f}^{1/2} - p_{\text{H}_2, p}^{1/2}) \equiv P_{\text{H}_2} (p_{\text{H}_2, f}^{1/2} - p_{\text{H}_2, p}^{1/2}) \quad (1)$$

which relates the hydrogen flux to the partial pressure of hydrogen (p_{H_2}) on the feed (f) and permeate (p) sides,



Sandwiched Liquid Metal Membrane (SLiMM)

Fig. 1 – Schematic of sandwiched liquid metal membrane (SLiMM).

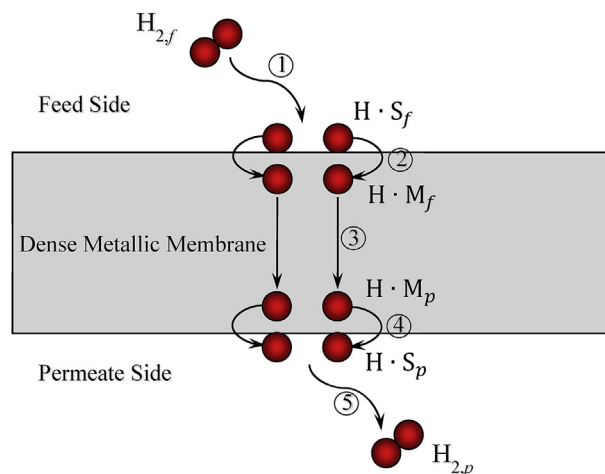


Fig. 2 – Schematic of the five steps of hydrogen diffusion through metal: (1) dissociative adsorption, (2) solution to the bulk, (3) diffusion, (4) dissolution to the surface, and (5) associative desorption.

membrane characteristics such as metal atom concentration (c_t) and maximum hydrogen solubility ($\chi_{\text{H-M},s}$), membrane thickness (δ), Sieverts' equilibrium constant (K_S), and diffusion coefficient (D_{H}). This simple relation is derived assuming that the diffusion step is the rate-determining step (RDS) in the sequence of steps, and that the hydrogen solubility is low, so that the interstitial mole fraction can be approximated via Sieverts' law, following a square-root dependence on hydrogen partial pressure, $\chi_{\text{H-M}} \approx K_S \sqrt{p_{\text{H}_2}/p^0}$, where p^0 is standard (atmospheric) pressure. These assumptions may not necessarily remain true under all conditions for the liquid metals of interest, and indeed have even been shown [22] to be invalid under certain conditions for palladium membranes, when the adsorption/desorption steps can be the RDS. While a framework has been developed to ascertain this [22], however, the solubility and diffusion parameters needed for the model for many metals, especially liquid metals, are unknown. Finally, although we are specifically interested here in the potential application of liquid metal-membranes, there are other applications of liquid metals as well where these parameters are of interest, e.g., as coolants in fast neutron reactors, in metal casting, and perhaps even in hydrogen storage [18].

One convenient way to determine some of these kinetic and thermodynamic parameters is by monitoring hydrogen uptake, or evolution, over a liquid metal pool in what is known as the Sieverts' apparatus [23,24]. This apparatus can be set up to operate in one of two different modes: 1) a constant-volume mode, known as a pressure Sieverts' apparatus [23], or 2) a constant-pressure mode, known as a volume Sieverts' apparatus [24]. Both modes of operation follow similar set-ups and theory, having the metal of interest of known surface area and volume within a closed system under hydrogen atmosphere that monitors either the system pressure at a constant volume (pressure Sieverts' apparatus), or the total system volume at a constant pressure (volume Sieverts' apparatus), so as to determine the amount of hydrogen permeating into the metal

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