Supporting Information

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Gallium Plasmonic Nanoantennas Unveiling Multiple Kinetics of Hydrogen Sensing, Storage, and Spillover

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§S1 Modeling the plasmonic response of Ga-H₂ interaction: an application of the Drude Model

In order to corroborate the change in the optical constants of Ga when exposed to molecular hydrogen (H₂), we have calculated the dielectric function of Ga when the density of free electrons is increased (H₂ has a donor character). The calculations are based on the Drude model for free electrons. With this model, the dielectric function can be expressed as

\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \] (1.a)

where

\[ \varepsilon_1(\omega) = \varepsilon_e - \frac{\omega_p^2}{\omega^2 - \frac{1}{\tau^2}} \quad \text{and} \quad \varepsilon_2(\omega) = \frac{\omega_p^2}{\omega\tau(\omega^2 - \frac{1}{\tau^2})}. \] (1.b)

\( \omega_p \), the plasma frequency and \( \tau \), the relaxation time are given by,

\[ \omega_p = \sqrt{\frac{Ne_e^2}{me_0}} \quad \tau = \frac{m}{\rho Ne_e^2} \] (2)

In (2), \( N \) is the free-electron density, \( m \) the electron mass, \( e \) the electron charge, \( \rho \) the resistivity of the material and \( \varepsilon_0 \) the vacuum dielectric permittivity.

Since above 2.5eV photon energy, liquid Ga has a Drude-like dielectric function,\(^1\) this has been fitted to a Drude model using the plasma frequency and the relaxation time as the fitting parameters. To model the increment of the number of free-electrons, the free-electron density obtained from the fitting of the experimental measurements in absence of H₂ has been increased by a factor \( n \) ranging between 1.0 (absence of H₂) and 1.5. Figure SI-1 shows the values of the real and imaginary parts of the dielectric function as a function of the factor \( n \).

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\(^1\) Losurdo, M., Suvorova, A., Rubanov, S., Hingerl, K., Brown, A. S. Thermally Stable Coexistence of Liquid and Solid Phases in Gallium Nanoparticles. Nat. Mater. 15, 995–1002 (2016).
Figure SI-1. (a) Real and (b) imaginary parts of the dielectric function of liquid Ga as the free-electron density is increased by a factor $n$. The black dots represent the experimental values. Inset in (a) shows the real part of the dielectric function at photon energies higher than 7eV to see how the Fröhlich frequency (black dashed line: $\text{Re}(\varepsilon)=-2$) evolves as a function of $n$.

Inset in Fig. SI-1(a) shows how the Fröhlich frequency condition ($\text{Re}(\varepsilon)=-2$) depends on $n$. This parameter corresponds to the excitation frequency of the LSPR (Localized Surface Plasmon Resonance) in isolated metallic particles whose radius is smaller than the wavelength. As the value of $n$ increases (electron density increases), this condition is met at higher photon energies i.e. the resonance peak is blue-shifted as the electron density increases. At the same time, an increment of absorption is observed as it is shown in Fig. SI-1(b) due to a decreasing of the relaxation time. This effect will result in an overall damping of the resonant peaks.

§S2: Modeling the Ga$_2$O$_3$ formation during the reverse spill-over effect.

During the reverse spill-over process, electromagnetically, we can assume that the electron density ($n$) inside the nanoparticle and the effective refractive index around the nanoparticle simultaneously increases due to the formation of the Ga$_2$O$_3$. Because the Ga$_2$O$_3$ is mostly formed in the interface between the particle and the substrate (see Fig. 3 main text), we have modeled this situation by considering an effective substrate that has a refractive index ($n_{\text{subs}}$) that takes values between that of Al$_2$O$_3$ and the oxide (1.78 vs 1.90). In addition, we have fixed an external refractive index ($n_{\text{ext}}$) to 1.1 to take into account further effects of the oxide formation. The parameters considered for Fig.2i of main text are:

| color of line in plot | $n$ | $n_{\text{ext}}$ | $n_{\text{subs}}$ |
§S3. Evidence of Ga NPs LPSR usual red-shift for sensing change of surrounding media refractive index

The same Ga NPs as in Fig. 1c were exposed to isopropanol, and the spectra in Figs SI-2 both in terms of energy and wavelength show the usual red-shift of both the LO-LSPR and TO-LSPR due to the change in the refractive index of the surrounding media, being the red-shift wavelength dependent and higher at longer wavelength, i.e., a higher sensitivity is obtained in the NIR range.

When we compare these data to the blue-shift observed in Fig. 2 of main manuscript upon hydrogenation, it can be inferred that the hydrogen sensing mechanism is based on an electronic mechanism rather than a change in the refractive index as explained in the main text.

| Material       | $\varepsilon_2$ | $\gamma$ | $\delta$ |
|----------------|-----------------|-----------|-----------|
| Dark blue      | 1.00            | 1.0       | 1.78      |
| Light blue     | 1.05            | 1.1       | 1.83      |
| Yellow         | 1.10            | 1.1       | 1.88      |
| Red            | 1.15            | 1.1       | 1.90      |

**Figure SI-2:** Spectra of the imaginary part of the dielectric function, $\varepsilon_2$, as a function of (a) photon energy and (b) wavelength for Ga NPs of the same Ga NPs as in Fig. 1b of main manuscript as grown (red curve) and during sensing isopropanol (blue curve) which has a refractive index of 1.38.
§4. Chemical evidences of the Ga-H bonds formation at 200<T<500°C

§4.1. FTIR Analysis

The sample exposed to hydrogen at temperatures > 300°C where irreversible modifications occur indicating that some hydrogen is in the sample were characterized by FTIR. A band at 2020 cm\(^{-1}\) appeared that was assigned to the stretching mode of Ga–H.\(^2\)

![FTIR Spectrum](image)

**Figure SI-3.** As-deposited (solid line) and 1 bar H\(_2\)-loaded (dashed line) FTIR spectra of Ga NPs, showing the broad band of Ga-H bonds.

§4.2. Raman Spectroscopy Analysis

The samples before and after hydrogenation have been measured with a LABRAM (Horiba) spectrometer using a 532 nm laser with an incident power of 1mW not to induce any sample modification by the local laser irradiation. In the range 670 – 770 cm\(^{-1}\) several polyspecies of GaGaH\(_2\), Ga\(_2\)H\(_4\), Ga\(_3\)H\(_6\)\(^3\) can occurr giving rise to the broad peak observed increasing with hydrogenation runs at T 300°C as shown in Fig. SI-4.

![Raman Spectrum](image)

\(^2\) A. Sebastia´ E. Collins, Miguel A. Baltana´s, and Adrian L. Bonivardi, Hydrogen Chemisorption on Gallium Oxide Polymorphs, *Langmair* 21, 962-970 (2005).

\(^3\) X. Wang and L. Andrews Infrared Spectra of Gallium Hydrides in Solid Hydrogen: GaH\(_1\),2,3, Ga2H2,4,6, and the GaH2,4– Anions, *J. Phys. Chem. A*, 107, 11371-11379 (2003).
Figure SI-4. Raman spectra of Ga NPs on sapphire substrate before and after runs of exposure to hydrogen at 300°C for 30 min.

§4.3 X-ray Photoelectron Spectroscopy (XPS) Analysis

![XPS spectra](image)

**Figure SI-5.** High-resolution XPS spectra of Ga 3d photoelectron core level before and after exposure to hydrogen of Ga NPs at T>200°C and at T<200°C after two reversible cycles of hydrogenation. The spectra show before hydrogenation the Ga core of the NPs with a shell of Ga₂O₃. After hydrogenation at T = 300°C for 15 min, as a consequence of the reactive step, a broadening of the peaks occurs because of the appearance of Ga-H bonds, and GaO-H bonds due to air exposure after hydrogenation during the transferring of the sample to the XPS system. For T<200°C, the relative amplitude of the GaO and Ga peaks shows a reduction of the native oxide shell component by the hydrogen (still some oxide is present because the analysis was done ex-situ), supporting the absence of any reactive step.

§4.4 Atomic Force Microscopy Analysis of the hydrogenated Ga NPs.

The AFM topography of the Ga NPs in Fig. SI-6 shows no variation of the morphology and therefore, neither etching nor erosion/damage of the nanoparticles for hydrogenation at T < 500°C.
**Figure SI-6.** AFM images of the small Ga NPs (left) and large Ga NPs (right) before and after hydrogenation, with the min indicators of the surface roughness parameters.

§S5. Stability of the hydrogenated Ga NPs system

The stability of samples after the hydrogen treatment has been checked after storing the samples in air in the laboratory for approximately 2 years. Figure SI-7 shows a sample hydrogenated at T= 300°C (a) and a sample hydrogenated at the extreme temperature of T = 600°C (b). Noteworthy, the samples hydrogenated at 300°C show stability of both plasmon resonance modes, whereas for the sample exposed to H₂ at 600°C both plasmon resonance modes decrease in amplitude and red-shift due to the interfacial Ga₂O₃ and reduction of the metallic Ga volume of the NP. The LO-LSPR mode is damped more than the TO-LSPR because of the associated electromagnetic field localized at the interface with support and because it probes more along the direction parallel to the support surface and, therefore, the interfacial Ga₂O₃.
**Figure SI-7**: Spectra of the imaginary part of the pseudodielectric function, $\langle \varepsilon_2 \rangle$, for Ga NPs as deposited (black line), after exposure to 1 Torr of H$_2$ at (a) 300°C for 10 cycles and at (b) 600°C (blue lines) and after 2 years of keeping the samples in air in the lab (after was treated by H$_2$ (red lines).

§S6. **Insight into the metallic interstitial hydrogen.**

In order to demonstrate that the interaction of hydrogen with Ga NPs at $T < 200°C$ is mainly metallic interstitial hydrogen, without any reactive step, we have monitored the kinetics also exposing the same Ga NPs under the same conditions to Helium (He) as shown in Fig SI-8. The kinetics was monitored recording the variation of the maximum of the plasmon resonance. The same fully reversible phenomenon was recorded for both hydrogen and He, supporting the non-reactive regime. While in the case of hydrogen the interaction is the interstitial incorporation of donor atomic hydrogen and the sensing is based on an electronic interaction as described in the main text, in the case of He it is interstitial diffusion and the sensing is based on the change of the refractive index of the medium (i.e. He in the surrounding and chemisorbing on the surface) and/or He interstitial diffusion slightly changing by volume expansion and incorporation the refractive index of the nanoparticles.

Additionally, on the basis of the similar shape of the kinetics for H$_2$ and He, the following consideration could be inferred for the selectivity to H$_2$ and He: For $T > 200°C$, the reactive regime and the non-reversibility of hydrogen allows the selectivity to hydrogen; for $T < 200°C$, i.e., in the non-reactive interstitial regime, it is possible to distinguish pure hydrogen from pure He on the basis of the different response rate (i.e. an order of magnitude faster for hydrogen); it would not be straightforward only optically to selectively distinguish H$_2$ from He in mixtures of both.
Figure SI-8: Real time monitoring of the kinetics of interaction and desorption of hydrogen compared to that of the unreactive He gas. In both cases, $T = 190^\circ$C and while the pressure for $H_2$ is 1 Torr, the pressure for He is 10 Torr.

§S7. Energetics of the Ga NP/Al$_2$O$_3$ interface plasmon catalysed hydrogen and oxygen spillover

The energetics and structures were obtained using the software Materials Studio 4.0 from Accelrys.

As sketched from the structures in Figure SI-9 and their corresponding energy levels calculated by density functional theory, the on-top positions for adatom absorption on a 1×1 Al-terminated $\alpha$-Al$_2$O$_3$(0001) surface are AlI and OI, whereas Al2, and O2 are in the second row and regarded as hollow positions. For high-surface coverage by Ga clusters ($\geq$ 1 ML) on the $\alpha$-Al$_2$O$_3$(0001), which is the present case, the configuration with the lowest energy surface ($E_{Ga} = -1.78$ eV) corresponds to Ga positioned at the on-top AlI sites (see green shadowed area in the structure sketch for Ga/Al$_2$O$_3$ in Fig. SI-9).$^4$ Similarly, calculations for a hydrogen-covered $\alpha$-Al$_2$O$_3$(0001) surface have shown that the minimum energy is also achieved with the hydrogen directly on top of the AlI site with a hydrogen chemisorption energy $E_{H} = -1.48$ eV$^5$ (green shadowed area in the structure sketch for H/Al$_2$O$_3$ in Fig. SI-9). Furthermore, Tepesch et al.$^5$ also calculated that when the H atom has to shift from the on-top AlI site to

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$^4$ Verdozzi, C., Jennison, D. R., Schultz, P. A., Sears, M. P. Sapphire (0001) Surface, Clean and with $d$-Metal Overlayers. *Phys. Rev. Lett.* 82, 799–802 (1999).

$^5$ Tepesch, P. D., Quong, A. A. First-Principles Calculations of $\alpha$-Alumina (0001) Surfaces Energies with and without Hydrogen. In *Computer Simulation of Materials at Atomic Level*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, FRG, 2005; pp 377–387.
the nearest O1 site, it has to cross two potential barriers - a lower one of 0.2 eV and a higher one of 0.6 eV - which inhibits the migration of H atoms over the α-Al2O3(0001) surface. From this we infer that when the Ga-Al2O3 interacts with hydrogen, the H and Ga compete for the on-top All sites. The chemisorption energy of an H atom onto a Ga atom in the Ga NP (-3.18 eV) (central sketch in Fig. SI-9) is similar to the chemisorption energy of H-on-Ga at the All site (green shadowed area in H/Ga/Al2O3 structure sketch in Fig. SI-9). Consequently, it is energetically feasible for hydrogen to spillover from the Ga NPs to the Al2O3 support where hydrogen occupies the All site, while the Ga atom moves to the hollow position on Al2 and is surrounded by O1 atoms, corresponding to an energy minimum. This initiates the interfacial interaction of Ga with oxygen from Al2O3, which further proceeds by hydrogen spillover and oxygen reverse spillover into Ga NP, causing the interfacial Ga2O3 domains seen in the Ga NPs (Fig. 3 main text) that produce the red-shift and damping observed in real time of the Ga LSPR. The plasmon photocatalyzed reverse oxygen spillover from the thermodynamically-stable α-Al2O3 has been recently demonstrated possible for other systems.

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6 Yang, R., Rendell, A. P. First Principles Study of Gallium Atom Adsorption on the α-Al2O3(0001) Surface. J. Phys. Chem. B 110, 9608–9618 (2006).
7 Filatova, E. O., Konashuk, A. S., Sakhonenkov, S. S., Sokolov, A. A., Afanas’ev, V. V. Re-Distribution of Oxygen at the Interface between γ-Al2O3 and TiN. Sci. Rep. 7, 4541 (2017).
Figure SI-9: Calculated chemisorption energies and corresponding sketches of structures for (a) H on clean $\alpha$-Al$_2$O$_3$(0001) (indicated as H/Al$_2$O$_3$), (b) Ga on clean $\alpha$-Al$_2$O$_3$(0001) (indicated as Ga/Al$_2$O$_3$), (c) H in Ga (the top and side views of the Ga unit cell with hydrogen are shown); (d) H on Ga-covered $\alpha$-Al$_2$O$_3$(0001) (which is the present experiment and indicated H/Ga/Al$_2$O$_3$) and (e) Ga on H-covered $\alpha$-Al$_2$O$_3$(0001) (indicated as Ga/H/Al$_2$O$_3$). The arrow in the plot simply guides the eye on the energetic driving force for the hydrogen spillover from the Ga site at the Ga NP to the Al$_2$O$_3$ support. The red and green shadowed areas identifies with respect to the Ga/H system configurations and structures of higher energy for the binary H/Al$_2$O$_3$ and Ga/Al$_2$O$_3$ compared to lower energies of the ternary-system H/Ga/Al$_2$O$_3$.

§S8. Role of the outer Ga$_2$O$_3$ shell in the interaction with H$_2$

Ga NPs are stabilized through the formation of an ultrathin Ga$_2$O$_3$ shell (~1nm)$^1,8$ consequently, the first step of the hydrogen/Ga NP interaction is the reduction of the oxide

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$^8$ Y. Gutiérrez, D. Ortiz, J. M. Sanz, J. M. Saiz, F. González, H. O. Everitt, F. Moreno, How an oxide shell affects the ultraviolet plasmonic behavior of Ga, Mg and Al nanostructures. Optics Express, 24 (2016).
shell with very fast kinetics (<10 s), also considering that dissociative adsorption of H₂ on Ga₂O₃ with the formation of OH and GaH species has been demonstrated. Ga₂O₃ surface sites have been reported to be active in the heterolytical dissociation of H₂ at T>700K to give Ga-H and O-H hydroxyl species. In order to prove the existence of a catalytic effect of Ga₂O₃ on the H₂ dissociation and consequently on the Ga₂O₃ removal, we first tried to desorb thermally the oxide by heating the Ga NPs samples in a He flow at various temperature in the range 200°C-700°C and monitoring in real time the changes of the Ga NPs plasmon resonance. The oxide shell was found to desorb thermally at 650°C.

The Ga NPs ensemble with the 1 nm Ga₂O₃ oxide shell we exposed to 1 Torr of H₂ at various temperatures and the LSPR was monitored by real-time spectroscopic ellipsometry. At temperatures of 100°C, 200°C, 300°C, 350°C no change in the plasmon resonance was observed, indicating that the oxide shell is still there inhibiting any dissociation of H₂ and further interaction with hydrogen. At T=400°C, a blue-shift and increase in amplitude of the plasmon resonance occurs (see Fig. SI-10) consistent with the oxide shell removal, as also supported by electromagnetic simulations (see also simulation paragraphs §S1-2). Therefore, at T=400°C, the first step of the hydrogen/Ga NP interaction is the reduction of this 1 nm Ga₂O₃ shell according to the overall reaction:

\[
\text{Ga}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Ga} + 3\text{H}_2\text{O}
\]  

The oxide-shell removal is a very fast process (under those conditions) occurring in less than 10s, as shown by Fig. SI-10b; here, the maximum in the extinction coefficient profile, k, correspond to the oxide removal end-point; after that the decrease of k indicates that once the oxide shell is removed other processes start (see manuscript discussion). The temperature of 400°C for the Ga₂O₃ thin shell reduction is consistent with previous studies that found the maximum Ga-H concentration on Ga₂O₃ reached above 650K.

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9 Pan, Y. X., Mei, D., Liu, C. J., Ge, Q. Hydrogen Adsorption on Ga₂O₃ Surface: A Combined Experimental and Computational Study. J. Phys. Chem. C 115, 10140-10146 (2011).
10 J. Vecchietti, M. A. Baltanás, C. Gervais, S. E. Collins, G. Blanco, O. Matz, M. Calatayud, A. Bonivardi, Insights on hydride formation over cerium-gallium mixed oxides: A mechanistic study for efficient H₂ dissociation. Journal of Catalysis 345, 258–269 (2017).
11 Y.-X. Pan, D. Mei, C.-j. Liu, Q. Ge, Hydrogen Adsorption on Ga₂O₃ Surface: A Combined Experimental and Computational Study. J. Phys. Chem. C 115, 10140–10146 (2011).
12 S. E. Collins, M. A. Baltanas, A. L. Bonivardi, Hydrogen Chemisorption on Gallium Oxide Polymorphs, Langmuir, 21, 962-970 (2005).
Indeed, the dissociation of molecular hydrogen has been reported to be a heterogeneous process catalyzed by the Ga$_2$O$_3$ itself, which could be represented as shown in the scheme (2)

$$
\begin{align*}
\text{O} \rightarrow \text{Ga} \rightarrow \text{O} + \text{H}_2 & \rightarrow \text{O} \rightarrow \text{Ga} \rightarrow \text{OH} + \text{H}_2 \\
\text{H} & \rightarrow \text{O} \rightarrow \text{Ga} \rightarrow \text{H} + \text{H}_2 \rightarrow \text{O} \rightarrow \text{Ga} \rightarrow \text{OH} + \text{H}_2 \\
\text{H}_2O & \rightarrow \text{H}_2O
\end{align*}
$$

(2)

where both the Ga and O surface site are involved in the dissociative chemisorption of hydrogen, with the plausible formation also of Ga-OH. As second step, the OH group and the H adatom of the GaH species can combine at 400°C to desorb water, which will create an oxygen vacancy.

The oxygen vacancies left by the water desorption favor the further H$_2$ dissociative adsorption and the production of GaH species, with a calculated energy barrier of 0.61 eV. Once the oxide is removed, the Ga NP interacts with hydrogen. Indeed, the formation of surface gallium hydride species from the reduction of the oxide is a key step for further H$_2$ dissociation at unsaturated Ga surface sites, thus decreasing the dissociation activation barrier.

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14 Y.-X. Pan, D. Mei, C.-J. Liu, Q. Ge, Hydrogen Adsorption on Ga$_2$O$_3$ Surface: A Combined Experimental and Computational Study, J. Phys. Chem. C, 115, 10140–10146 (2011)

15 Vecchietti, J.; Collins, S.; Xu, W.; Barrio, L.; Stacchiola, D.; Calatayud, M.; Tielens, F.; Delgado, J. J., Bonivardi, A. Surface Reduction Mechanism of Cerium–Gallium Mixed Oxides with Enhanced Redox Properties. J. Phys. Chem. C 117, 8822–8831 (2013).
Figure SI-10: (a) Ga NPs before (red curve) and after exposure to 5Torr H₂ at 400°C for 20s. The blue-shift is consistent with the oxide shell removal. (b) Oxide removal kinetics observed by recording the real-time variation of $k$ (extinction coefficient) during exposure to H₂ at the sampling photon energy of approximately 3.5 eV, which is the maximum of the plasmon resonance.

§9. Noise and sensitivity by Dielectric function amplitude change of the LSPR

The evaluation of the experimental noise is critical especially in the context of limit of detection (LoD). Since we have quantified the LoD by the change of the amplitude of the plasmon resonance, we show in Fig. SI-11 a typical kinetic plot of the variation of the dielectric function of the Ga NPs (sample from Fig. 1d of main text) during vacuum (base pressure of $10^{-8}$ Torr) in the reactor, and after introducing 5 μTorr of H₂. The noise on $\varepsilon_2$ is of the order of 0.01. Therefore, any variation of the amplitude of $\varepsilon_2$ at the LSPR higher than 0.01 is meaningful. Furthermore, it can also be noted from Figs. SI-6-7 that the Ga NPs sensor is extremely stable throughout the measurement.

Figure SI-11. (a) Variation of the amplitude of TO-LSPR during exposure of Ga NPs (sample from Fig. 1 of main text) in vacuum and under exposure to 5 μTorr. The red-shaded area denotes the noise level of ±0.01 $\varepsilon_2$ during both vacuum and hydrogen exposure. (b) A stable $\varepsilon_2$ signal is observed in vacuum over 30 min.
§10. Hydrogen Diffusivity in liquid Gallium compared to other metals

Data of diffusivity of hydrogen in liquid/molten metals have been collected from various sources in literature and are compared to gallium in Table SI-1.

Table SI-1: Hydrogen diffusivity, $D_H = D_{0,H} \exp \left( -\frac{E_D}{RT} \right) \text{cm}^2/\text{s}$

| Parameter/ Liquid Metal | $E_D$ (kJ/mol) | $D_{H,0}$ (cm$^2$/s) | $\Delta S^{o}_D$ (J/mol K) | $\Delta H^{o}s$ (kJ/mol) | $\Delta S^{o}_S$ (J/mol K) |
|-------------------------|----------------|-----------------------|---------------------------|--------------------------|-----------------------------|
| Ga                      | 10.1 [a]       | 9.61 [b]              | 8.63x10$^{-4}$ [a]        | -29.9 [a]                | 27 [a]                      |
|                         |                | 3x10$^{-3}$ [b]       | @17-273 °C                |                          | -47.3 [a]                   |
| Pd                      | 27.0 [c]       | 23.62 [d]             | 2.83x10$^{-2}$ [c]        | +2.3 [c]                 | -10.6 [c]                   |
|                         |                | 2.9x10$^{-3}$ [d]     | @170-290°C                |                          | -58.2 [c]                   |

[a] P.S. Yen, Supported Liquid Metal Membranes for Hydrogen Separation. PhD Thesis, Worcester Polytechnic Institute, 2016.
[b] S.N. Mazayev, Y. G. Prokofiev, Journal of Nuclear Materials, 212-21, 1497-1498 (1994).
[c] N.D. Deveau, Y. H. Ma, R. Datta, Journal of Membrane Science, 437, 298-311 (2013).
[d] T. Genjiro, Journal of The Research Institute for Catalysis Hokkaido University, 6, 13-19 (1958)

$D_H$ is the interstitial diffusion coefficient of atomic hydrogen, cm$^2$/s$^{-1}$

$D_{H,0}$ is the pre-exponential interstitial diffusion coefficient of atomic hydrogen, cm$^2$/s$^{-1}$

$E_D$ is activation energy of interstitial diffusion of H

$\Delta S^{o}_D$ is standard entropy change of activation for diffusion

$\Delta S^{o}_S$ is standard entropy change of hydrogen solution in metal

$\Delta H^{o}s$ is standard enthalpy change of hydrogen solution in metal

Note that the hydrogen solubility in liquid gallium is an endothermic process differently from hydrogen in palladium that is an exothermic process.

Comparing Pd and liquid Ga, the hydrogen diffusivity in liquid Ga is about 7 times higher than Pd ($D_{H, Ga} = 6.68x10^{-4}$ cm$^2$/s; $D_{H,Pd} = 9.33 \times 10^{-5}$ cm$^2$/s) at 500°C. The hydrogen solubility at 550 °C, $\chi_H$/Ga-atoms = 2nH$_2$ /nGa-atoms = 2 × 8 ×10$^{-3}$ /1.85 ×10$^{-3}$ = 8.7. This provides roughly 8 H atoms per Ga atom at atmospheric pressure of H$_2$, which is a very high solubility, likely explained by the significant vacancies present in a liquid metal. Other attractive features of Ga are the low melting point, hydrogen diffusivity even at room temperature, low volatility and non-toxicity.

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16 Pei-Shan Yen, Nicholas D. Deveau, and Ravindra Datta, Dissociative Adsorption, Dissolution, and Diffusion of Hydrogen in Liquid Metal Membranes. A Phenomenological Model. : Ind. Eng. Chem. Res. 57, 1607–1620 (2018).