# Mathematical Modeling of Hydrogen Spillover on Metal-Doped Carbon Materials

## EGEE 520 (Derek Elsworth)

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Hydrogen spillover can greatly enhance hydrogen storage capacity at ambient conditions. However, the mechanism of hydrogen spillover onto carbon-based materials is still not clear. We present here a study of hydrogen diffusion behavior on Pt-doped graphite using Infinite Element Analysis method. The hydrogen diffusion coefficient is calculated and diffusion time is estimated. The model is helpful for further spillover mechanism studies.

## Introduction

Hydrogen is one of the best alternative fuels for fuel cell powered vehicles [1]. However, for realization of such a hydrogen fuel economy, there remains a key barrier that must be overcome, hydrogen storage. So far, no materials currently exist can meet the DOE's goal for on-board vehicular hydrogen storage.

Recently, some studies[2-4] have proved that small amounts of transition metal/metal oxides may activate certain storage materials, such that synergistic effects can create new adsorption sites and enhance hydrogen uptake at ambient temperatures. The activation has been explained with the concept of spillover. Hydrogen spillover has long been observed in catalysis field[5], which is defined as the dissociative chemisorption of hydrogen on the metal and the subsequent migration of atomic hydrogen onto the surface of the support such as alumina, carbon and so on[6] that would not typically adsorb active species under the same conditions.
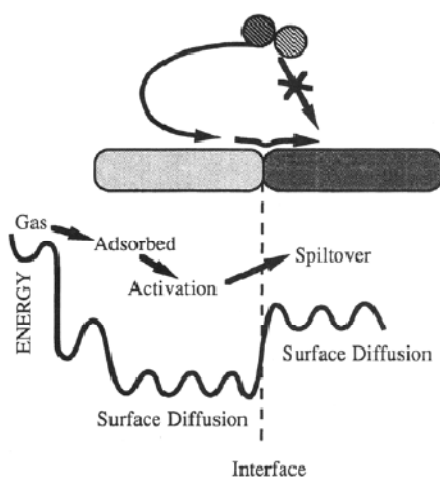


Fig.1. Schematic representation of spillover of a gaseous diatomic from an adsorbing onto a nonadsorbing surface[5]

The nature of the spiltover hydrogen and the kinetics of hydrogen spillover have been investigated[7-12]. And mathematic models have been presented for spillover to provide the framework to move beyond "trial and error" optimization of hydrogen adsorption on metal doped materials. The main approaches to model hydrogen spillover include: Chemical kinetics model[13, 14], dimensional analysis[5](or Langmuiran ), Monte Carlo analysis[15-18] and density function theory (DFT)[12, 19-21]. In the classic chemical kinetics model, a hydrogen molecule dissociates on a surface atom and the dissociated species is then free to migrate to the support. The analysis of the chemical kinetics of the complete hydrogen spillover process leads to complex expressions with several rate parameters which are difficult to determine experimentally. To simplify the analysis, a rate determining step is commonly assumed and the overall reaction rate is tied to a single

equation or single step which apparently limits the application of the model. Dimensional analysis may help in overcoming experimental limitations for determination individual rate parameters. In the analysis, hydrogen spillover is modeled as a three-dimensional flow system. Taking all factors important for hydrogen spillover, an expression can be developed with arbitrary exponential constants which used to correlate experimental data. A Monte Carlo stochastic simulation was developed based on Ziff-Gulari-Barshad (ZGB) method commonly used in heterogeneous catalysis. The reactions are represented by a group of probability functions. It allows analyzing the full spillover process using an idealized surface with systematic variations of the surface in a way that is not possible in the laboratory. DFT is a quantum mechanical theory used to investigate the state of molecules and condensed phases. It has been used to calculate the binding energy of hydrogen and metal atoms, the chemical states of spiltover hydrogen, effect of metal on dissociation of hydrogen, etc.

In this study, finite element analyis will serve to explore the hydrogen diffusion behavior on metal doped carbon materials with interests in the following aspects: (1) hydrogen diffusion time estimation, (2) diffusion coefficient calculation, (3) the effect of interfacial length of metal-support contact, and (4) the activation energy and adsorption energy.

## 2.1 Governing equations

There are three steps in the hydrogen spillover process: 1) Hydrogen molecules dissociate to hydrogen atoms on the surface of the metal Pt and form Pt-H bonds; 2) After all empty positions on the surface of the metal have been taken, hydrogen atoms will diffuse from the metal to the carbon surface due to concentration difference (surface diffusion from metal to carbon); 3) hydrogen atoms will subsequently diffuse on the carbon surface and be adsorbed in the micropores of the graphite (surface diffusion from carbon to carbon).

In this model, a graphite surface cell containing 50 x 50 carbon atoms, with a dimension of 12.2 nm x 12.2 nm is used for modeling. In each cell, there is one single Pt atom (Diameter = 2nm) placed in the middle. The average sphere of diffusion for graphite receptor depends on the ratio of Pt/C and the connectivity of platinum particle and graphite substrate. The two-dimension schematic plot is shown in Fig. 2.
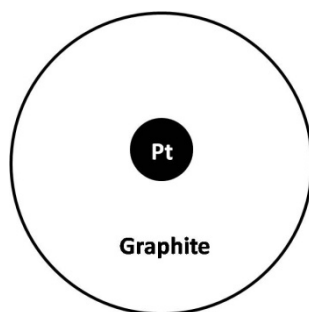


Fig. 2. Two-dimension plot of sphere model for hydrogen spillover on graphite.

As hydrogen diffusion is a continually changing state process, Fick's second law fits our modeling. The fluid flow and diffusion equation is:

$$A\frac{\partial c}{\partial t} + \nabla \cdot (-D\nabla c) = R$$

Here, A is time-scaling coefficient, c is concentration, D is diffusion coefficient, R is reaction rate. In our model, R is used as adsorption rate.

The initial and boundary conditions are such that the surface is initially clean and after time zero, hydrogen is equilibrated in the center of Pt and undergoes diffusion to the sphere that is bounded by $R_1$. r denotes the radial distance from the center of the Pt source.

$c = 0$, $r = 0$, $t > 0$; $c = aC_0$, $r = a$, $t > 0$; $c = rf(r)$, $0 < r < a$, $t = 0$

$C_0$ is the constant concentration at the surface of Pt sphere, a is the characteristic radius of activated carbon for spiltover hydrogen atoms, and f(r) is the initial distribution or zero.

## 2.2 Formulation

The hydrogen adsorption condition is set at room temperature (25 $^{\circ}$C).

Comsol diffusion model (transient analysis) is applied to analyze the process.

$$\delta_{ts}\frac{\partial c}{\partial t} + \nabla \cdot (-D\nabla c) = R$$

Another important equation for diffusion coefficient calculation is Arrehenius expression.

$$D = D_o \exp(-\frac{E_a}{kT})$$

$D_o$ is surface diffusivity at zero loading, $E_a$ is activation energy for surface diffusion, k is Boltzmann constant and T is absolute temperature.

## 2.3 Solution

2.3.1 Diffusion time

Fig.3 shows the diffusion process with a function of time. At a very short time period (0.0001s), hydrogen dissociates and diffuses on the metal surface. At about 0.1 second, hydrogen begins to diffuse from metal to carbon surface. Then due to the low diffusion coefficient, hydrogen diffuses slowly on the graphite surface. At about 150 s, the diffusion process completes.
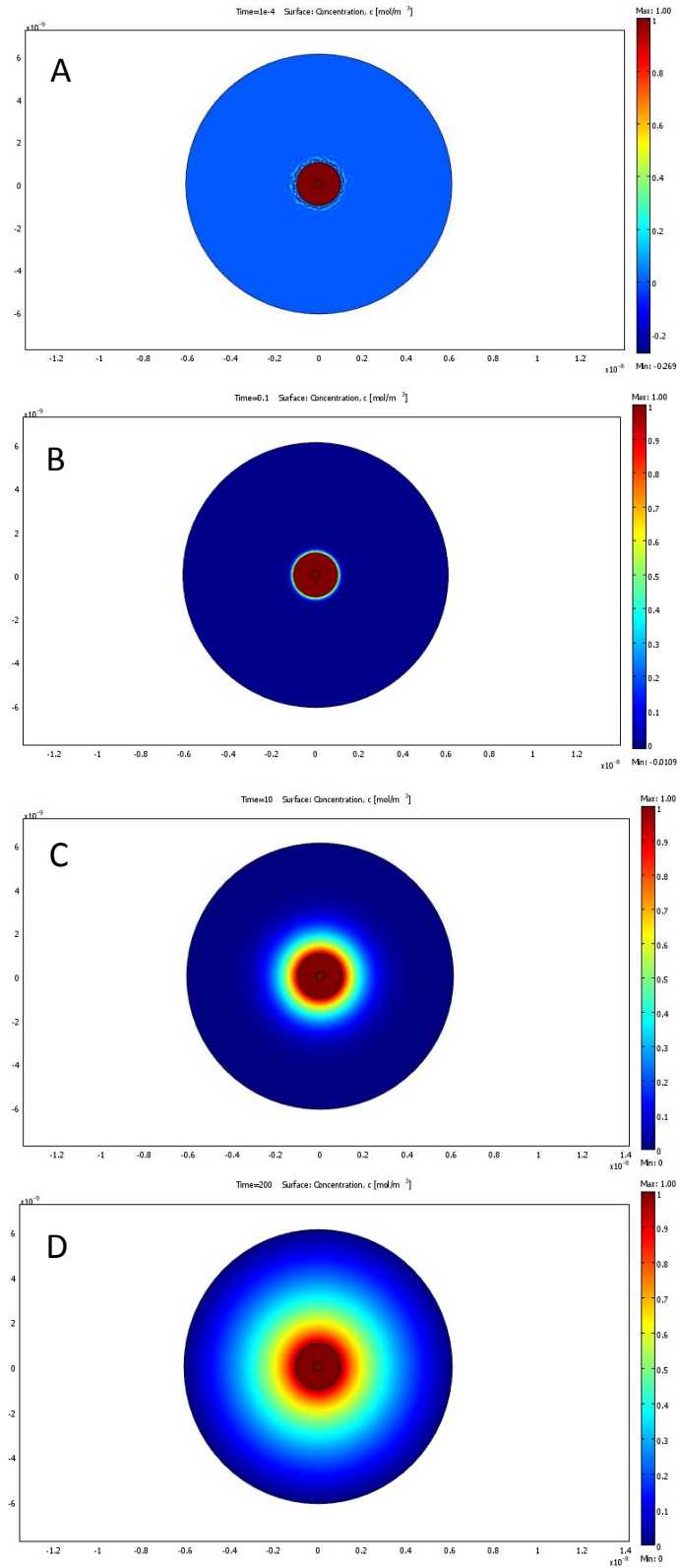
Fig. 3. Diffusion process with a function of time. A) 0.0001 s; B) 0.1 s; C)10 s; D)200 s.

## 2.3.2 Diffusion concentration change rate

It is very clear (Fig.4) that the hydrogen diffusion concentration change rate (the slope of the plot) decrease as time increases.
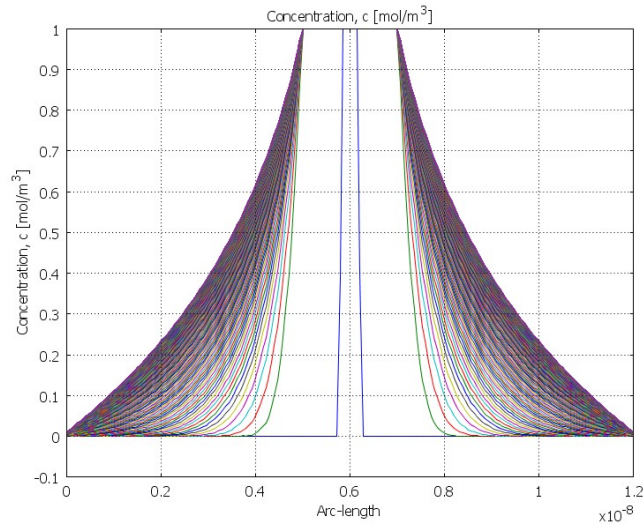


Fig.4. Cross-section plots as time increases from 0 to 200 s. Y axis is hydrogen diffusion concentration, x axis is diffusion distance.

## 2.3.3 Hydrogen diffusion (from metal to carbon) coefficient
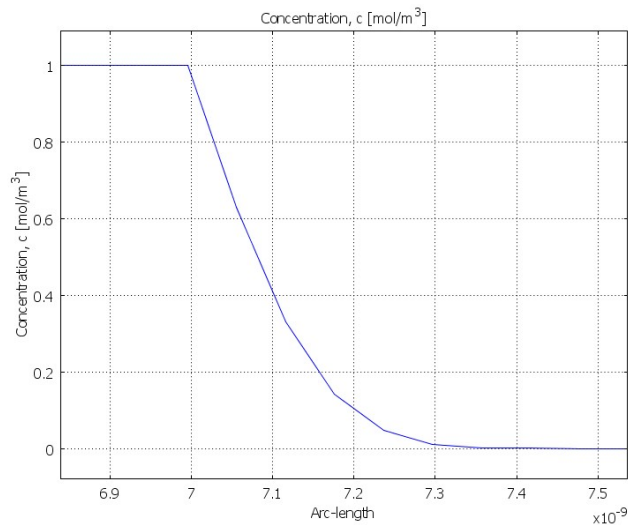


Fig.5. Cross-section plot at time 0.1 s

Fig.5 can be used to estimate hydrogen diffusion coefficient. At 0.1 s, hydrogen just began to diffuse on the graphite surface. The diffusion distance (from metal to carbon) is about $0.4 \times 10^{-9}$ m (from Fig.5). Therefore, the spillover area can be calculated:

$$\pi[(0.1 \times 10^{-8} + 0.4 \times 10^{-9})^2 - (0.1 \times 10^{-8})^2] = 3 \times 10^{-18}\,\text{m}^2$$

Then, the diffusion (spillover) coefficient = 3 x $10^{-18}$ m$^2$/0.1 s= 3 x $10^{-17}$ m$^2$/s.

The above calculation proves that hydrogen diffusion (spillover) coefficient is a function of diffusion distance and diffusion time. Therefore, we can conclude that if the doped metal amount is constant, when we reduce the doped particle size, i.e. increase the interfacial length of metal-support contact, the diffusion coefficient will increase.

## 3 Validation

To compare our Comsol modeling result with the literature[22], four platinum particles were arranged on the graphite background. Hydrogen diffusion steady state after 200 s is shown in Fig.6a. Fig.6a and Fig.6b have similar hydrogen concentration distribution.
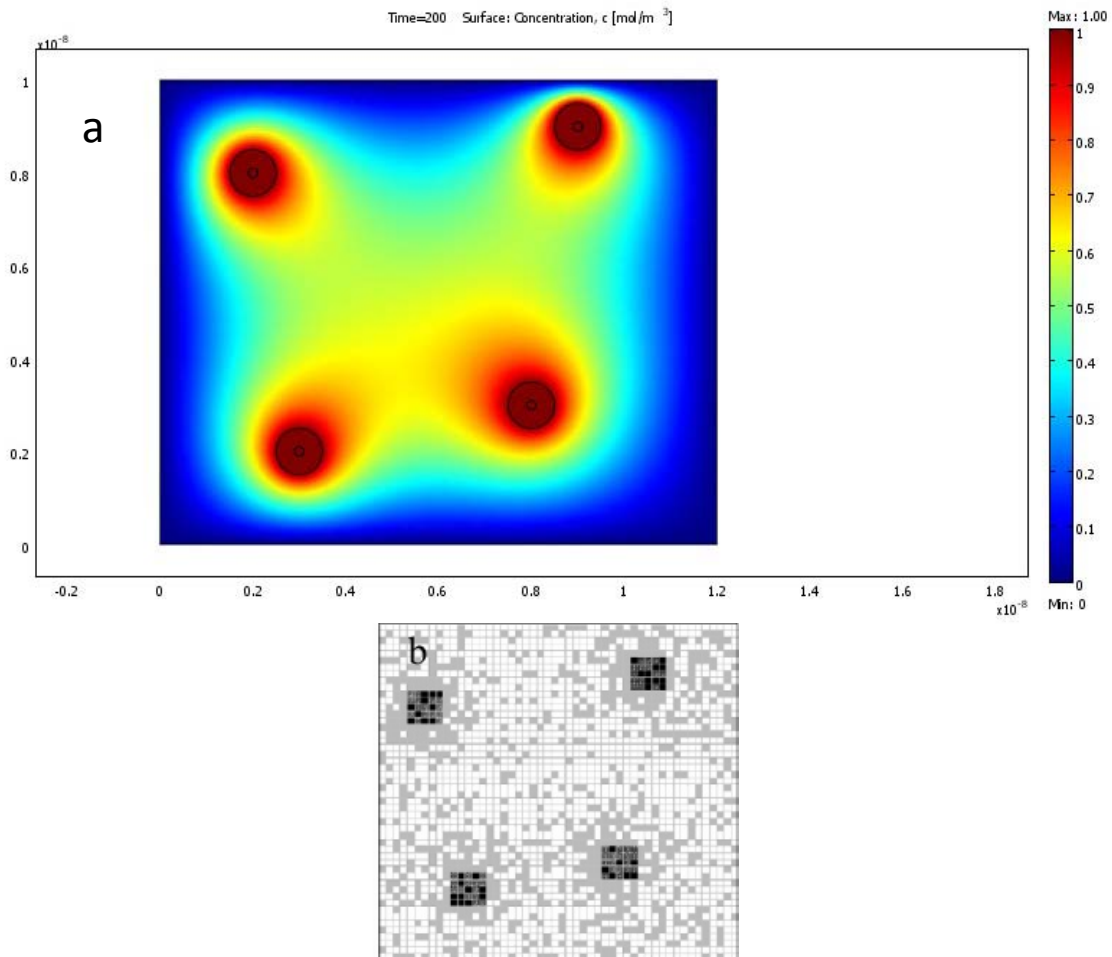


Fig.6. Comsol simulation a) and Monte Monte Carlo simulations b) at steady state. In b), Metal and support sites are denoted by black and white coloration, respectively. Sites filled with hydrogen are shown in gray.

## 4 Parametric study

4.1 Hydrogen surface diffusion from metal to metal

Transport of adsorbed species across a chemically uniform surface is commonly referred to as surface diffusion. The rate of this process depends on the strength of the interaction between the adsorbed species and the surface [23].Sladek et al. reported diffusion coefficient of hydrogen on Pt and concluded the following equation to calculate the diffusion coefficient of hydrogen on Pt at different temperatures:

$D = 1.6 \times 10^{-2} \exp(-0.45 \, q/mRT) \, cm^2/s$

Where q is heat of adsorption, for Pt, it can be found in the reference [21]. m is a number chosen for each type of bond to give the best fit of absolute values of D when plotted against $q/mRT$ . For H/Pt system, m=3[17]. Large diffusion coefficients have been obtained from this equation, i.e. $10^{-6}$ cm$^2$/s for hydrogen on Pt at 333-348 K with activation energy of 5.7 kcal/mol. For our system, hydrogen diffusion coefficient on Pt is calculated to be 3.6 x $10^{-6}$ cm$^2$/s at room temperature (298.15 K).

4.2 Hydrogen surface diffusion from carbon to carbon

In our system, graphite is served as acceptors in hydrogen spillover. Compared with diffusion coefficient of hydrogen on Pt, hydrogen diffusion coefficient on carbon is small. Boudart et al. [24] measured net hydrogen adsorption for a Pt/carbon system and modeled the resulting data to arrive at a surface diffusion coefficient from carbon to carbon of 3.4 x $10^{-19}$cm$^2$/sand 5.8 x 10 $^{-17}$cm$^2$/sat 300 °C and 392 °C, respectively.  But it is believed they underestimated the diffusion coefficient based on our calculation. We used the following Arrehenius expression,

$D = D_0 ex \, p\left(-\frac{E_a}{kT}\right) cm^2/s$

And calculated the activation energy of their system to be 179.1 kJ/mol which is too large to be true. In the above equation, $D_0$ is the surface diffusivity at zero loading, $E_a$ is the activation energy for surface diffusion, $k$ is Boltzmann constant (1.38 x $10^{-23}$ J/K), and T is absolute temperature. $D_0$ and $E_a$ are constants in a given system.

Causey, et al.[25]developed a relation

$D = 1.2 exp\left(-\frac{0.9eV}{kT}\right) cm^2/s$

to calculate hydrogen diffusion coefficient on graphite. The calculated activation energy 0.9 eV is validated by Chen, et al. [21]. By Causey's diffusion relation, the diffusion coefficient in our modeling is 7.58x $10^{-16}$ cm$^2$/s at room temperature.

R is the adsorption rate in our modeling with a unit of mol/ ($m^3 \cdot s$). It is used because when hydrogen active species diffuse on graphite surface, some of them will be adsorbed. R is used to show this diffusion and adsorption relation. We assume that after hydrogen concentration is lower than certain value, hydrogen adsorption will stop. Therefore, hydrogen adsorption time is always smaller than diffusion time.

$$R = -a \times c \times \text{flc1hs(b-t,0)/b}$$

a is the ratio of hydrogen adsorption concentration to diffusion concentration. c is the diffusion concentration. flc1hs is a step function which is applied to show the adsorption process. b is the adsorption time. After time b, hydrogen adsorption will shut off. a is obtained from our experiment data with a value of 0.0015. b is set to be 100 s (if the diffusion time is 150 s). This empirical equation is proved to accord with the experiment results.

The parameters and constants used in our modeling are summarized in table 1 and table 2.

Table 1 Parameters

| Name | Expression | Value |
|---|---|---|
| Diffusion coefficient (from metal to metal) | D | $3.6*10^{-10}$ $m^2/s$ |
| Diffusion coefficient (from carbon to carbon) | D | $7.58*10^{-20}$ $m^2/s$ |
| Adsorption coefficient | a | 0.0015 |
| Original concentration (in the center of Pt) | c0 | 1 mol/$m^2$ |
| Concentration ratio | c/ c0 | variable |

Table 2 constants

| A | T | Ea (metal) | Ea (carbon) | m |
|---|---|---|---|---|
| 1 | 298.15 K | 0.40 | 0.78 | 3 |

## 5. Conclusion

1) Infinite element analysis is a useful method for the analysis of hydrogen spillover process. Comsol diffusion model (transient analysis) can be applied to this process.
2) In our modeling, the whole hydrogen diffusion process takes about 150 seconds which can help to set the adsorption time intervals for hydrogen adsorption experiments.
3) Hydrogen spillover (diffusion from metal to carbon) coefficient is calculated for the first time. In our system, it is $3 \times 10^{-17}$ $m^2/s$.
4) The increase of doped metal dispersion will increase the spillover coefficient.
5) The modeling result agrees well with the literature result.

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