Solution of Inverse Thermal Problem for Assessment of Thermal Parameters of Engineered H_2 Storage Materials

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Abstract: New materials for hydrogen storage application require accurate thermal parameters estimation to be efficiently used in practice. The task of material characterization has been formulated as inverse thermal problem of parameter estimation from a few thermal measurement experiments. The forward problem that models thermal measurement experiment has been implemented in COMSOL. The backward problem has been solved using Global Optimization Matlab toolbox with additional acceleration strategy based on smooth parametric reconstruction of objective function manifold. The results show that the addition of Expanded Natural Graphite (ENG) 'worms' followed by compaction introduces a thermal conductivity anisotropy with the lower value of the thermal conductivity in the direction from which the compaction load was applied. The increase in thermal conductivity by adding ENG 'worms' was strongly material dependent: Sodium Aluminum Hydride > mixture of Lithium Amide and Magnesium Hydride > Metal Organic Framework-5

Keywords: thermal inverse problem, global optimization, hydrogen storage materials

1. Introduction

The Hydrogen Storage Engineering Center of Excellence focuses on the development of alternative, materials based methods for H_2 storage for light duty vehicles that need to meet challenging system performance targets [1] that have been developed by the FreedomCAR and Fuel Partnership. On-board reversible (complex) metal hydrides form one class of H_2 storage materials for such a system. The metal hydride is integrated with heat transfer surfaces in order to reject the heat of H_2 absorption at a high rate which is set by the refueling time target. This typically requires fin and tube heat exchangers in which the metal hydride has been interdispersed between the fins. An alternative approach is to mix metal hydride materials with materials that enhance the thermal conductivity and to compact the composite material through uniaxial compaction in order to obtain a H_2 storage system with a low volume. Compaction of the composite material can cause thermal conductivity anisotropy due to the alignment of the thermal conductivity enhancing phase in a preferred direction [2]. Quantifying the thermal conductivity anisotropy of H_2 is the purpose of the COMSOL model that will be discussed in this work. It poses a classical Inverse Thermal Problem that is very demanding computationally and prone to non-unique solution [3]. Previously the common approach was the reduction of number of indentified thermal parameters and usage of reduced and/or simplified physical models [4, 5].

The Inverse Thermal Problem is solved using COMSOL as a forward solver for realistic 3D transient thermal model of experiment, Figure1, running under Matlab optimizer *patternsearch* that implements derivative free direct search algorithm [5].

2. Materials and Thermal Measurements

Three materials, Ti-doped sodium aluminum hydride (SAH), an 8:3 mixture of Lithium Hydride and Magnesium Amide (LAMH), and a Metal Organic Framework (MOF-5, produced by BASF and provided by Ford) have been mixed with expanded natural graphite 'worms', kindly provided by SGL Carbon, and uniaxially pressed in a square die in order to compact the material in cube shaped samples that were suitable for thermal conductivity measurements with a Hot Disk Thermal Constants Analyzer (Fig.1). The analyzer supplies a constant power to an initially isothermal sample via a sensor that is located in the middle between two cube shaped samples and follows during a limited heating period the resulting temperature increase by using the same sensor also as a resistance thermometer. The time traces of the change in temperature are recorded and made available to the COMSOL model developed in this study in order to quantify the thermal conductivity anisotropy. The thermal conductivity measurements were conducted in the axial direction of the sample (direction from which the compaction load was applied) and perpendicular to the axial direction by simply turning the cube shaped sample sideways and repeating the measurement. The two sets of data served as input to the COMSOL model. For the case of MOF5 material with 10 wt.% ENG 'worms', three separate measurements along three perpendicular directions have been taken and used as input for the inverse problem.

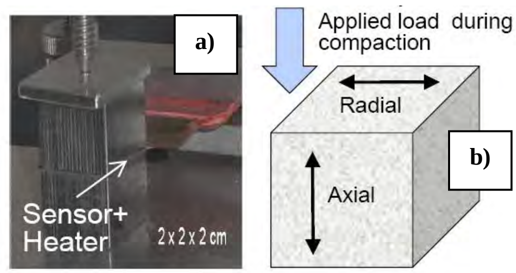

Figure 1. a) Thermal measurement system and b) Material compaction process.

3. Forward Problem Formulation and Parameters Selection

In similar hot disc heating experiments [4], inverse problem of thermal parameter identification had been solved using an analytical solution for the hot disc in infinite media. This approach becomes prohibitive for material exhibiting anisotropic properties. It also does not allow inclusion of the heat transfer coefficient for the boundary between the sensor and the material. The latter becomes important for the materials modified by the applied stress as it results in different contact surface properties. Unaccounted it leads to the wrong relation between the heat applied from the hot disc and the heat transfer properties of the material. Another shortcoming is that only thermal diffusivity can be estimated from the analytical model [5]. The heat capacity must be measured in a separate experiment. Therefore, here, reasonable detailed physical model has been used for material parameters identification.

The complete experiment is modeled by two partial differential equations: Eq. (1) for the 3D temperature distribution inside the bulk material and Eq. (2) for the 2D temperature distribution in the heating sensor, which was modeled as a thin object with thermal flux conditions. Eq. (3) represents the boundary condition at the interface between the sensor and the surface of the bulk material.

$$\rho_{sample} \cdot C_{sample} \cdot \frac{\partial T_{sample}}{\partial t} + \nabla\left(-k_{sample} \cdot \nabla T_{sample}\right) = 0 \qquad (1)$$

$$\rho_{sensor} \cdot C_{sensor} \cdot d_{sensor} \cdot \frac{\partial T_{sensor}}{\partial t} + \nabla\left(-d_{sensor} \cdot k_{sensor} \cdot \nabla T_{sensor}\right) =$$

$$d_{sensor} \cdot q + h \cdot \left(\mathrm{T_{sample}} - \mathrm{T_{sensor}}\right) \qquad (2)$$

$$-\boldsymbol{n} \cdot \left(-k_{sample} \cdot \nabla T_{sample}\right) = h \cdot \left(-T_{sample} + T_{sensor}\right) \qquad (3)$$

The outside material surface is kept under the constant ambient temperature. Zero heat flux conditions have been imposed on the surfaces of symmetry.

Altogether, a single experiment requires 6 parameters $q, k_{sensor}, C_{sensor}, h, k_{sample}, C_{sample}$ for complete description. If applied heat q can be reliably measured the number of parameters can be reduced to 5. Addition of another measurement from perpendicular direction adds the new parameters $h_i, {}_i k_{sample}$ for identification. Thus, working with two perpendicular measurements 7 parameters have to be identified and three perpendicular measurements increase this number to 9. Assuming the sensor properties stay the same for all measurement k_{sensor}, C_{sensor} can be identified from all prior available measurement and kept fixed reducing the number of parameters to 5 and 7 respectively.

4. Implementation of forward problem in Comsol

As the number of parameters that need to be determined is sufficiently large, special care has to be taken to reduce the run time for the forward problem.

Comsol implementation of eq. (1-3) consists of 3D General Heat Transfer transient model for the bulk material and 2D Thin Conductive Shell model for the heating sensor interacting through the boundary condition (3).

Computational grid shown on the Fig.2 consists of 2560 hexahedral elements with exponentially changing density away from the heater. A boundary layer has been organized close to the edge of the heating circle using Comsol Mapped Mesh capabilities.

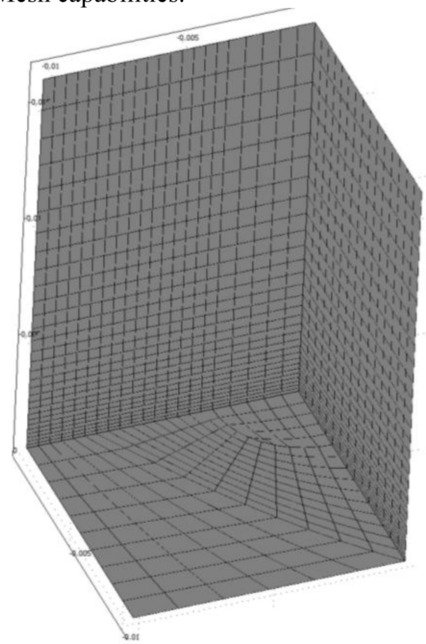

Figure 2. Fully structured computational mesh.

Typical transient solution of 200 steps shown on the Fig.2 takes 7 seconds using parallel Comsol solver on 4 Intel(R) Xeon(R) 2.67GHz processors computer.

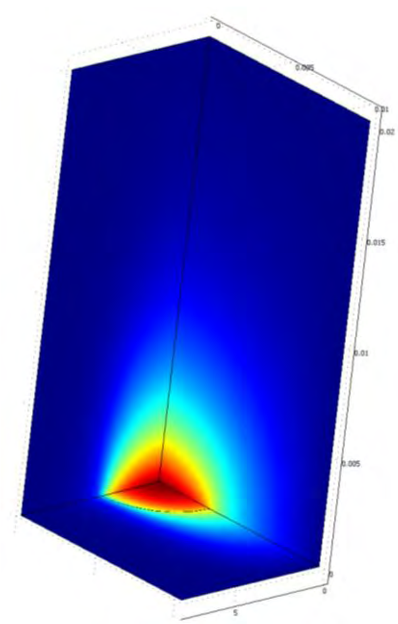

Figure 3. Solution of the forward problem after 5 seconds of heating. Only ¼ of the physical domain has been modeled.

5. Backward problem

A Matlab script has been written using two (Fig.4) or three Comsol models for the forward problem to contribute to the objective function:

$$Objective = \sum_{models\, i} \sum_{j_{start}}^{j_{end}} \left(\langle T_{\exp\, i}(t_j) \rangle - \langle T_{\mathrm{model}\, i}(t_j) \rangle \right)^2 \tag{4}$$

$$\langle T_{model\, i}(t_j) \rangle = \frac{1}{S} \int_{Sensor} T_{model\, i}(t_j)\, ds$$

Only part of the time curves has been used for evaluating the objective function. The j_{end} has been selected short enough to guarantee that the temperature on the outside boundaries is equal to $T_{ambient}$. j_{start} has been selected for small noise in heat starting to die out.

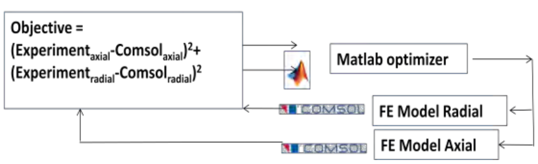

Figure 4. Schematics of interaction between Matlab optimizer and solving the backward problem and Comsol solving the forward problem.

Experimentation with different Matlab optimization algorithms has shown that the whole family of gradient techniques provides worse results in terms of resulting fitting error than non-gradient search algorithms. In other words, at the time when optimizer stops the error given by the gradient algorithms is higher.

The best results have been achieved with *patternsearch* that implements derivative free direct search algorithm [5]. The technique is very robust, quickly converges to the vicinity of the minimum, does not require calculation of derivatives and allow work with different norms. The major problem of this approach is that it is very slow for certain type of objective function landscapes such as long narrow valleys once the vicinity of the minimum has been reached. Unfortunately, this is the case for the thermal problem that attempts to evaluate many parameters at once when variation of some of them results in opposite trends that compensate each other.

It is, therefore, highly desirable to find some acceleration strategy of the derivative free direct search algorithms.

6. Acceleration strategy of direct search algorithms

Here, an amendment of existing algorithm with gradient type techniques is suggested when the smooth trend of the parameter changes has been calculated using dynamics of parameter data accumulated over sufficiently long number of optimizer steps.

Figure 5 demonstrates linear and quadratic smoothing of parameter change dynamics in course of *patternsearch* run on a 5 parameter inverse thermal model.

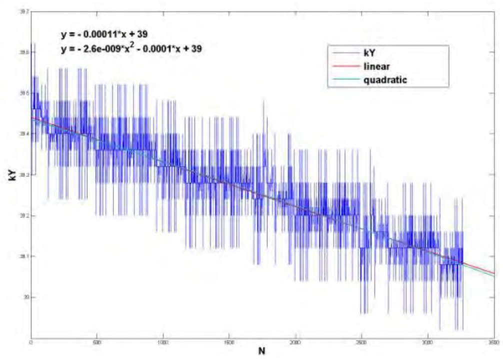

Figure 5. Typical dynamics of a parameter change in course of *patternsearch* work parameterized with the number of steps.

Acceleration is achieved by a large leap that follows the smooth parameter trend. A typical case would require from 3 to 15 of such leap steps and tremendously accelerates the convergence. The most expensive part of this approach is to accumulate enough data for the smooth trend to be reliably calculated. The length of this trend in terms of number of iteration steps of the direct search algorithm and the leap size specifying the projected objective function drop (Fig.6) are adjustable parameters of this approach. They are problem specific and have to be determined from a few test runs at the beginning of the studies or adaptively change during the progress of optimization.

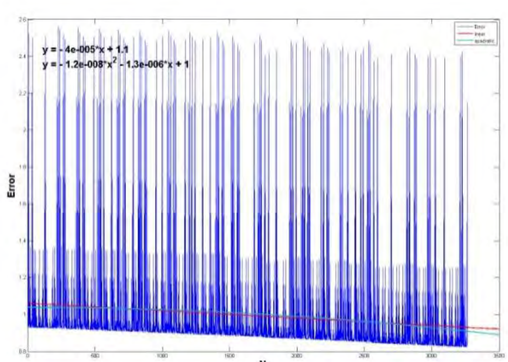

Figure 6. Dynamics of objective function drop in course of *patternsearch* work parameterized with the number of steps. The size to the leap step in terms of the number of the *patternsearch* steps is determined by requesting the desired drop of the objective function. Note that requesting zero value is not the best choice as the minimum could be missed. The optimal value is determined by the line search along the smoothed parameter manifold parameterized by the *patternsearch* steps.

7. Results

Figs. 7-9 show an example of inverse parameters estimation for two different compounds subjected to axial compression (Fig.1). Local minima have been found characterized by higher error residual. Some parameters have very similar values for the best solution and for the local minima but some vary quite considerably – Fig.8 for heat capacity and Fig.9 for the heat transfer coefficients between the heating disc and the sample. Apparently certain degree of compensation is possible in the thermal system described by Eqs. (1-3).

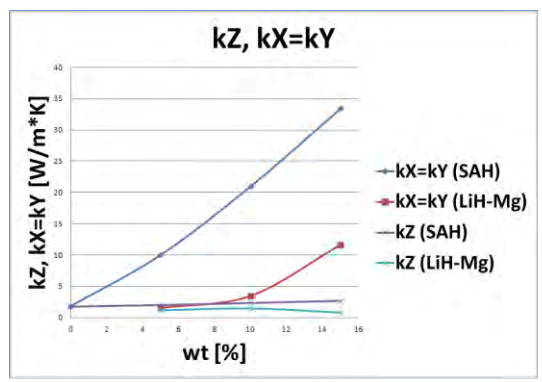

Figure 7. Thermal conductivities.

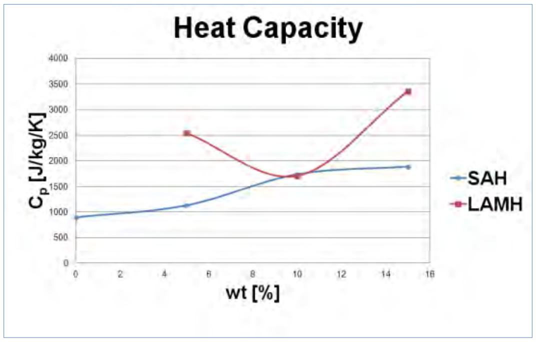

Figure 8. Heat capacity.

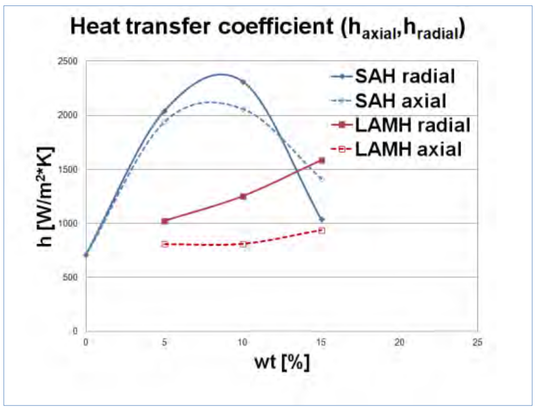

Figure 9. Heat transfer coefficients between the hot disk and the sample.

Fig.10 shows the difference between the Comsol model and the measurements. Most of the error concentrates in the initial period of the heating process implying that the hot disc sensor model is too crude in that time interval. However, the influence of that beyond 0.5 second is minimal. Selection of j_{start} discussed in the Section 5 allows to eliminate the sensor parameters from considerations.

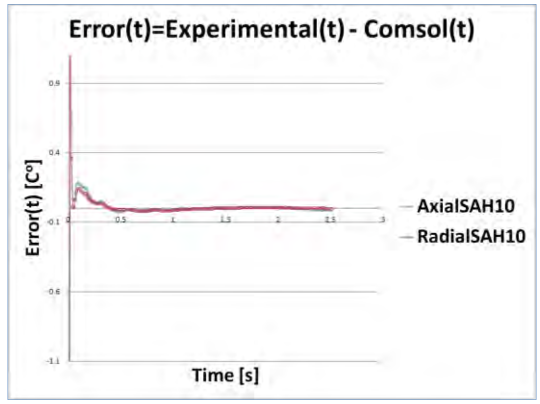

Figure 10. The difference between Comsol model and experimental measurements.

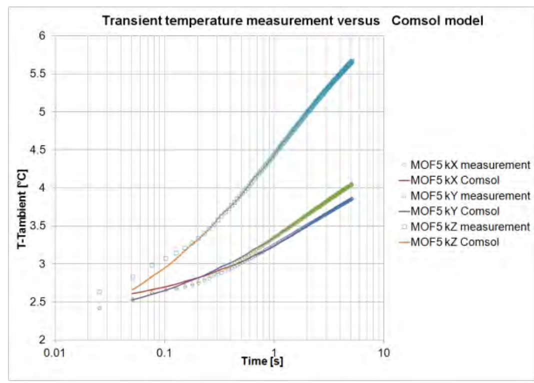

Figure 11. Experimental measurements versus Comsol inverse problem solution for MOF5 compound when three time traces of measurements in all perpendicular directions have been used in objective function.

Fig.11 demonstrates considerable improvement in solution of inverse thermal problem upon increasing amount of experimental data used in objective function from 2 to 3 traces taken in all perpendicular direction. Constraint of kX=kY has been lifted in that case which also contributed to the accuracy of the fit.

The thermal parameters identified from solution of inverse problem are summarized in the Table 1.

Table 1. Thermal parameters identified using three thermal measurements in all perpendicular directions for MOF5 compound with 10 wt.% ENG 'worms'.

Parameter	Unit	Value
kZ	W/(m.K)	0.287
kX	W/(m.K)	3.658
kY	W/(m.K)	1.71
Cp	J/(kg.K)	1148.9
h1	W/(m2.K)	650.6
h2	W/(m2.K)	700.5
h3	W/(m2.K)	799.3

In this case 10 wt.% ENG 'worms' had been added to the MOF-5 powder and the resulting anisotropy is due to the preferential orientation of graphite platelets under the applied axial stress. Improved thermal conductivity and compaction is important for engineering a hydrogen storage system that is based on hydrogen adsorption at cryogenic temperatures on materials like MOF-5 or MaxSorb.

Important question remains about impact of uncertainties in the experimental setup on the accuracy of the inverse problem solution. It has been determined that a small variation of starting time delay as well as dissipated power might decrease the error norm.

8. Conclusions

In this work the inverse problem of thermal parameter identification for the new material for hydrogen storage application has been solved using Comsol running under Matlab global optimizer.

A method for acceleration of global direct search optimization has been suggested based on the smooth parameterization of objective function manifold using accumulated residual data.

9. References

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