Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Coordinate the public access of select models developed under the Hydrogen Storage Engineering Center of Excellence (HSECoE) activity, including web posting of documentation and tracking downloads and web activity.
- Maintain performance of existing storage system models and update and validate as new experimental data becomes available.
- Enhance and expand existing models to improve simulation speed and application to other uses. This will focus on expanding the parameterization of the models and their flexibility in evaluating new material candidates. This will initially include the development of preprocessor sizing routines for the adsorbent and chemical hydrogen systems followed by the metal hydride and cryo-compressed systems.

Fiscal Year (FY) 2018 Objectives

- Work with HSECoE partners to continue to update and improve models developed by the center. Make these models available and accessible to the broader research and academic community through a controlled web-based access portal and track downloads and website activity.
- Create stand-alone executable versions of the HSECoE-developed material storage models to provide first-order storage system estimates based on material property information.
- Update the hydrogen storage equations with additional, alternative theoretical storage system formulations to allow users to choose the most appropriate theory for their material.
- Develop tools to size/design storage systems based on available volume or desired hydrogen storage mass.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- System Weight and Volume
- System Cost
- Efficiency
- Charging/Discharging Rates
- Dispensing Technology
- Systems Life-Cycle Assessments.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

Technical Targets

This project is conducting simulation and modeling studies of advanced onboard materials-based hydrogen storage technologies. Insights gleaned from these studies are being applied toward the hydrogen storage vessel design and materials synthesis that meet the following DOE 2020 hydrogen storage targets for light-duty vehicles:

- Storage system cost: \$333/kg $H_{2\ Stored}$
- System gravimetric capacity: 0.045 kg H_2/kg system
- System volumetric capacity: 0.030 kg H_2/L system
- Charging/discharging rates: 3–5 min
- Well to power plant efficiency: 60%.

FY 2018 Accomplishments

- Developed a metal hydride (MH) design tool that predicts system mass and volume based on thermodynamic and kinetic properties and developed it into an executable file; uploaded the model to the hsecoe.org website.
- Used the metal hydride design tool to predict the system mass for a recently developed metal hydride and compare it to sodium alanate.
- Developed a volume-based chemical hydrogen storage design tool that predicts the mass of hydrogen available based on the volume of the hydrogen storage system.
- Used the chemical hydrogen storage design tool to predict the system mass for an ammonia borane/boric acid mixture and compare it to ammonia borane alone.
- Developed an adsorbent design tool based on the UNILAN adsorption theory to give users the option of using either Dubinin-Astakov (D-A) or UNILAN as the basis for their hydrogen storage system formulation.
- Developed a volume-based adsorbent hydrogen storage design tool that predicts the mass of hydrogen available based on the total system storage volume available.
- Updated the adsorbent system design tools to include room temperature, cold, and cryogenic temperature system design capabilities.
- Tracked and monitored web activity and downloads.
- Developed and sent out a survey to users who had downloaded models from the website to find out how the models are being used and gather suggestions.

INTRODUCTION

Overcoming challenges associated with onboard hydrogen storage is critical to the widespread adoption of hydrogen-fueled vehicles. The overarching challenge is identifying a means to store enough hydrogen onboard to enable a driving range greater than 300 miles within vehicle-related packaging, cost, safety, and performance constraints. As new hydrogen storage materials are discovered and created, material developers must predict their full-scale vehicle performance and compare their performance with pure hydrogen storage (700 bar, cryo-compressed, and liquid hydrogen storage). The goal of this work is to provide material developers with the modeling tools necessary to make these predictions based on the work done by the HSECoE.

APPROACH

The approach for FY 2018 is to complete updates, validate, enhance, troubleshoot, de-bug, and document these models developed by the HSECoE so that they can be made accessible to and useful for other researchers within the hydrogen storage community. During subsequent years, these models will be updated with alternative storage system formulations, such as different isotherm models for adsorbents and alternative chemical reaction kinetic expressions for chemical hydrogen storage (CH) materials. In addition, stand-alone system design tools that do not require special software will be developed to serve as scoping tools for the new hydrogen storage materials that may be developed.

RESULTS

The following provides results from work completed this year by the multi-lab team with a focus on implementing volume-based storage system design tools while updating their counterparts that were based on a required mass of hydrogen. The team maintained public access of select HSECoE models, documented activities in several publications, and exercised the tools with other material data sets. The team also monitored and tracked web activity and model downloads. To date there have been 225 downloads of the tank volume/cost model, 158 downloads of the framework model, 101 downloads of the MH finite element model, 65 downloads of the MH acceptability envelope, 26 downloads of the CH system design standalone, and 24 downloads of the adsorbent system design standalone.

Metal Hydride Design Tool

As with the previously developed adsorbent and CH system design tools, the newly developed MH design tool uses the thermodynamic and transport properties of a MH to estimate the storage system mass and volume. Like the previous models, the input data for the MH comes from an Excel spreadsheet and the model results are returned to another spreadsheet. This will help materials researchers understand how their materials compare to the DOE technical targets.

The first step of this process is to calculate the equilibrium pressure of the hydride based on the van't Hoff equation:

$$P_{H2} = exp[(\Delta H - T\Delta S)/RT]$$

If the equilibrium pressure is greater than the required 5 bar at the temperature of the fuel cell waste heat (approximately 85°C), the additional complexity of a hydrogen burner to release the hydrogen is not required. If the burner is needed, it is added to the balance of plant and the hydrogen needed to overcome the reaction enthalpy will be added to the assumed usable hydrogen. The model then estimates the cooling tube spacing during refueling based on the HSECoE's Metal Hydride Acceptability Envelope. After calculating the mass of MH needed to supply the hydrogen, the total volume and mass of the material interior to the tank can be estimated. The model then uses a MATLAB version of the tank volume/cost model (or Tankinator model) to design the tank that would be used to enclose the MH. These calculations, along with the balance of plant components, are then used to estimate the overall system mass and volume that can be compared to the DOE technical targets.

The MH stand-alone design tool was evaluated by comparing the predicted system mass of a nano-confined lithium nitride storage material that has been developed by Dr. Vitalie Stavila at Sandia National Laboratories with the more conventional MH sodium borohydride. The model was also used to determine what material parameters should be modified to improve nano-Li_3N system-level gravimetric capacity, with the analysis results shown in Table 1. The initial nano-Li_3N properties predicted a much larger system mass than $NaAlH_4$ despite having a higher hydrogen capacity and similar thermal conductivity and density. The model also demonstrated that small changes in entropy result in higher temperatures needed to drive off the hydrogen, thus requiring a thicker and heavier aluminum tank. As a result, the overall system mass and volume are higher despite the lower hydride mass. By increasing the entropy from -104 to -109.7 kJ/mol/K while leaving all other inputs the same, the model predicts that the system mass of both materials will be the same. Dr. Stavila also developed a KH-doped nano- Li_3N with a higher capacity, thermal conductivity, entropy, and enthalpy. The system mass predicted by this new material was nearly identical to the baseline $NaAlH_4$. These results were shared with Dr. Stavila to provide direction to his material development. This modeling effort demonstrates the utility of the stand-alone metal hydride model in providing a quick screening process for developing metal hydrides.

Volume-Based CH Storage Stand-Alone Design Tool

The stand-alone CH storage system design tool was originally developed to estimate the total system volume and mass based on the desired usable hydrogen. Rather than building a vehicle around the hydrogen storage system, many designers have a limited volume and need to know the resulting capacity and range. Thus, the stand-alone CH storage design tool was modified to provide this capability, for both mass-based and volume-based design. The design parameters can then be used in the framework and a total range estimated for a particular system volume. This design tool was used in conjunction with the CH model in the framework to estimate the vehicle range as a function of storage system volume for both ammonia borane and alane, as shown in Figure 1.

CH Modeling with Newly Available Data

Purdue University had demonstrated that 20 wt% boric acid added to ammonia borane is a promising additive to decrease onset temperature as well as enhance the hydrogen release kinetics for thermolysis of ammonia borane. Working with researcher Hyan Tae Hwang, the data from this study performed in 2013 were evaluated with the CH models. The AB/BA hydrogen generation data, measured in a batch reactor up to 85°C at a rise of 1°C/minute, were simulated using Avrami kinetics with an overall reaction enthalpy based on boric acid dehydrating to metaboric acid combined with the decomposition of ammonia borane to produce hydrogen. The ammonia borane/boric acid mixture was assumed to be slurried with mineral oil as a 50/50 mixture to produce a flowable fluid that could be used in the exothermic AB model. Using the previously developed design tool coupled with the framework model, the system components and the total system mass and volume were estimated and then the framework was run using the US06 drive cycle.

The model predicted improved reaction kinetics resulting in a very small reactor required to achieve full conversion. However, it also demonstrated that the material has a lower hydrogen capacity once it is mixed with mineral oil to create a slurry. As a result, the larger volume of CH required produces a larger system mass and volume than with ammonia borane alone despite the faster kinetics and smaller reactor.

Table 1. Comparison of System Mass and Volume for nano-Li_3N to $NaAlH_4$

Inputs	NaAlH4	nano-Li3N system			KH doped nano-Li3N
Hydride Carrying capacity	0.056	0.062	0.086	0.062	0.065
Thermal Conductivty of Hydride Bed (with ENG)	9	8.9	8.9	8.9	10.3
Density of Hydride Bed (bulk)	720	675	675	675	720
Enthalpy per mole H2	-42000	-43100	-43100	-43100	-43900
Entropy	-124	-104	-104	-109.7	-115
Outputs					
System mass (kg)	331	432	331	330	339
System volume (m3)	0.38	0.42	0.32	0.29	0.35
Total Hydride Mass (kg)	125	113	82	113	108
Percentage of DOE 2020 Gravimetric Target (%)	38	29	38	38	37
Percentage of DOE 2020 Volumetric Target (%)	49	45	59	64	53
Notes		baseline case	H2 capacity predicting same system mass as NaAlH4	entropy predicting same system mass as NaAlH4	KH doped nano-Li3N

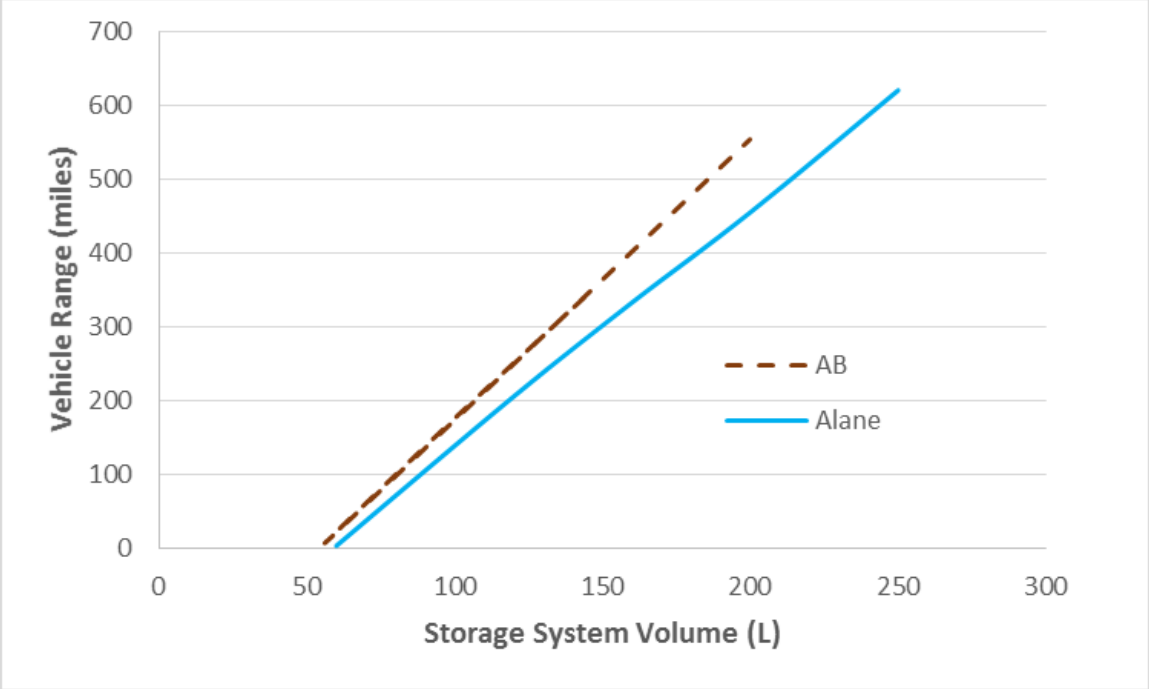

Figure 1. Vehicle range achievable for varying storage system volumes—AB and alane

Stand-Alone Adsorbent Design Tool with UNILAN Adsorption Theory

The existing stand-alone adsorption hydrogen storage system design tool is based on the D-A adsorption theory. However, not all adsorbents can be modeled well using D-A. For this reason, the stand-alone adsorption system design tool was augmented to use the UNILAN adsorption theory as an alternative basis, which describes the excess adsorption based on the following equation:

$$n_{ex} = \frac{n_{max}RT}{E_{max} - E_{min}} ln\left[\frac{exp(-\Delta S_0/R) + \frac{P}{P_0}exp\left(E_{max}/_{RT}\right)}{exp(-\Delta S_0/R) + \frac{P}{P_0}exp\left(E_{min}/_{RT}\right)}\right] - cV_a$$

where: E_{max} and E_{min} = the maximum and minimum values of $-\Delta H_0$ ($|\Delta H_0|$ is the isosteric heat) [J/mol]. $-\Delta H_0$ is uniformly distributed between E_{min} and E_{max}.

P_0 = Standard pressure [10^5 Pa] = 1 bar

R = Gas constant [8.314 J/mol-K]

ΔS_0 = Entropy change relative to a standard pressure of P_0 [J/mol-K]

≈ -8R for hydrogen

≈ -9.5R for methane

n_{max} = Maximum coverage [mol_gas/kg_ads]

T = Temperature [K]

MOF-5 hydrogen adsorption data was used to compare the two formulations, which showed agreement within 2% of the experimental data and within 0.1% of each other.

Additional Stand-Alone Adsorbent Design Tool Updates

Several updates have been completed for the existing stand-alone adsorption hydrogen storage system design tool. One such addition is to offer volume-based storage system design. Specifically, the original adsorbent design tool used the usable hydrogen storage as the basis for designing the entire hydrogen storage system. Similar to the CH model described above, this updated version uses the maximum total volume available for the hydrogen storage system as the basis for design. Starting with the maximum total storage volume available and the operating conditions, the storage system is designed inward by accounting for the balance of plant, pressure vessel, internal heat exchanger, and the remaining volume available for the adsorbent. The results from this design method are the total hydrogen capacity and range based on the initial volume constraint.

The final adsorption storage system design tool update is the balance of plant, which has now been augmented to account for room temperature (25°C), cold gas (200 K), and cryogenic temperature (77 K) operation. While many components perform the same tasks, their mass, volume, and cost are very different when designed to operate at different temperatures. Also, cryogenic operations require much more heat transfer capabilities and more stringent insulation requirements than the room temperature operations do. By comparison, cold gas operations are a mixture of the two extreme cases and, as such, can take advantage of some of the benefits of each. The stand-alone adsorption hydrogen storage system design tool now has all three operation condition choices for each of the adsorption theory formulations (D-A and UNILAN) and each of the design bases (target hydrogen mass or maximum total available volume).

User Survey

The team was tasked with obtaining a better understanding of who is using the models developed by the HSECoE, how they can be improved, and who may be willing to collaborate with us to provide experimental data. To this end, we reviewed and finalized a SurveyMonkey questionnaire and in December sent it to the user list obtained from those downloading models from the hsecoe.org website. The user list contained 229

unique emails; 11 of those emails were not functional. We received 24 responses (about 10%), with 5 answering yes to being open to work with us to evaluate the performance of their material. Figure 2 is an example result showing that most are using the models in an academic setting followed by industrial use.

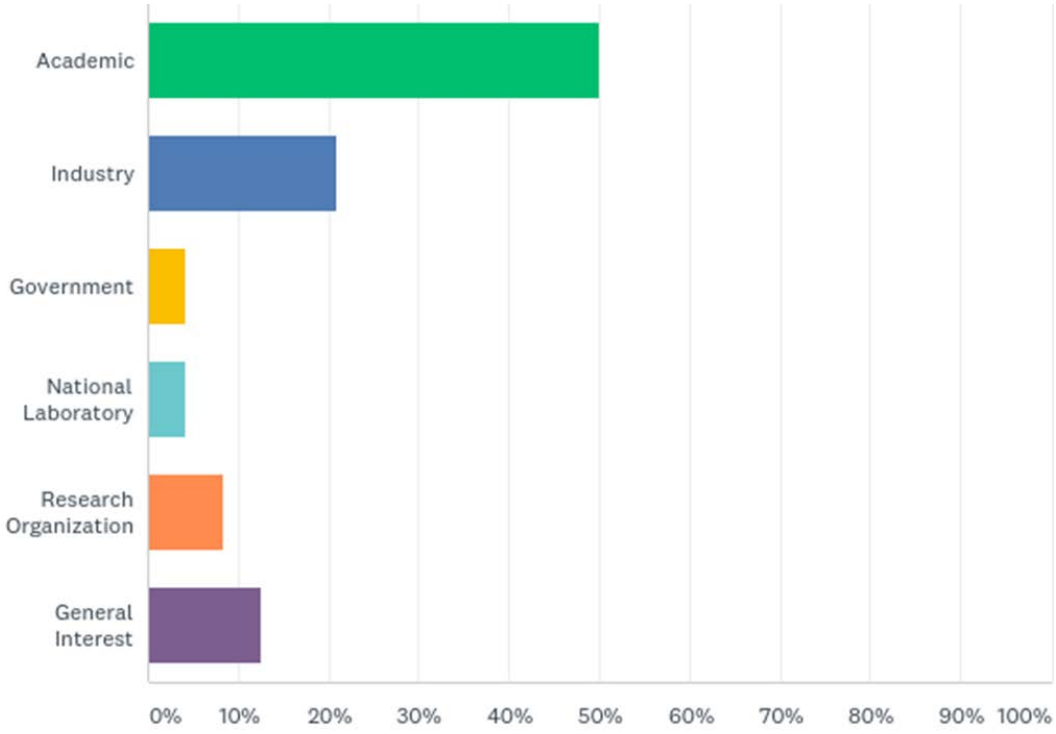

Figure 2. Survey results showing institutional setting for those using the models

The models currently developed and maintained by the team are listed in Table 2. These are either available on the website already or are in the process of being added for public download.

Table 2. HSECoE Models Available on Web Portal and Model Posting Status

Model Name	Lead	Status
MH Acceptability Envelope	SRNL	Complete
MH Finite Element Model	SRNL	Complete
Tank Volume/Cost Model	PNNL	Complete
MH Framework Model	SRNL	Complete
CH Framework Model	PNNL	Complete
Adsorption Data (AD) Framework Model	SRNL	Complete
AD Finite Element Model	SRNL	Model Complete[a]
Adsorption Data Fitting Routine	SRNL	Model Complete[a]
AD Stand-Alone System Design Tool	SRNL	Complete
CH Stand-Alone System Design Tool	PNNL	Complete

[a] Awaiting user's manual completion before the model is released to the public.

The models are made available publicly through the HSECoE web page, where website activity and model downloads are tracked. Figure 3 shows the latest website activity over the three-month period from July through September of 2018. The site received 139 visitors during this time, 85% of which were new visitors. Visitor sessions lasted an average of 4 minutes and 18 seconds and averaged 4.5 pages per visit. Figures 4 and 5 provide the user flows for the site and user origin cities, respectively.

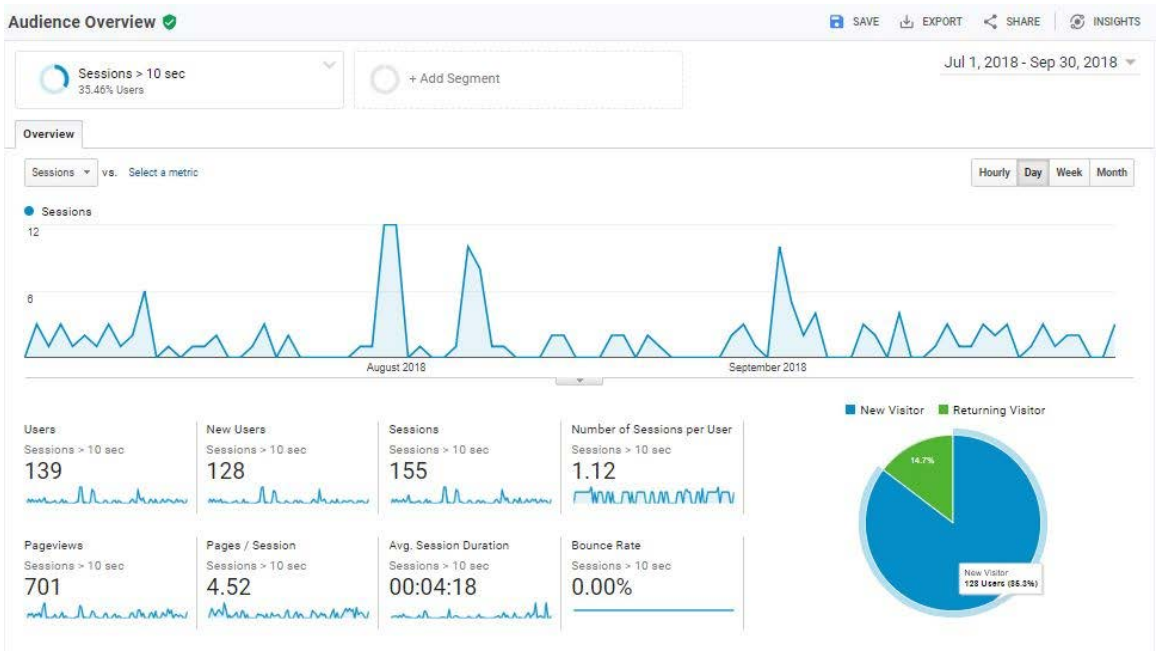

Figure 3. HSECoE web analytics: three-month site activity metrics

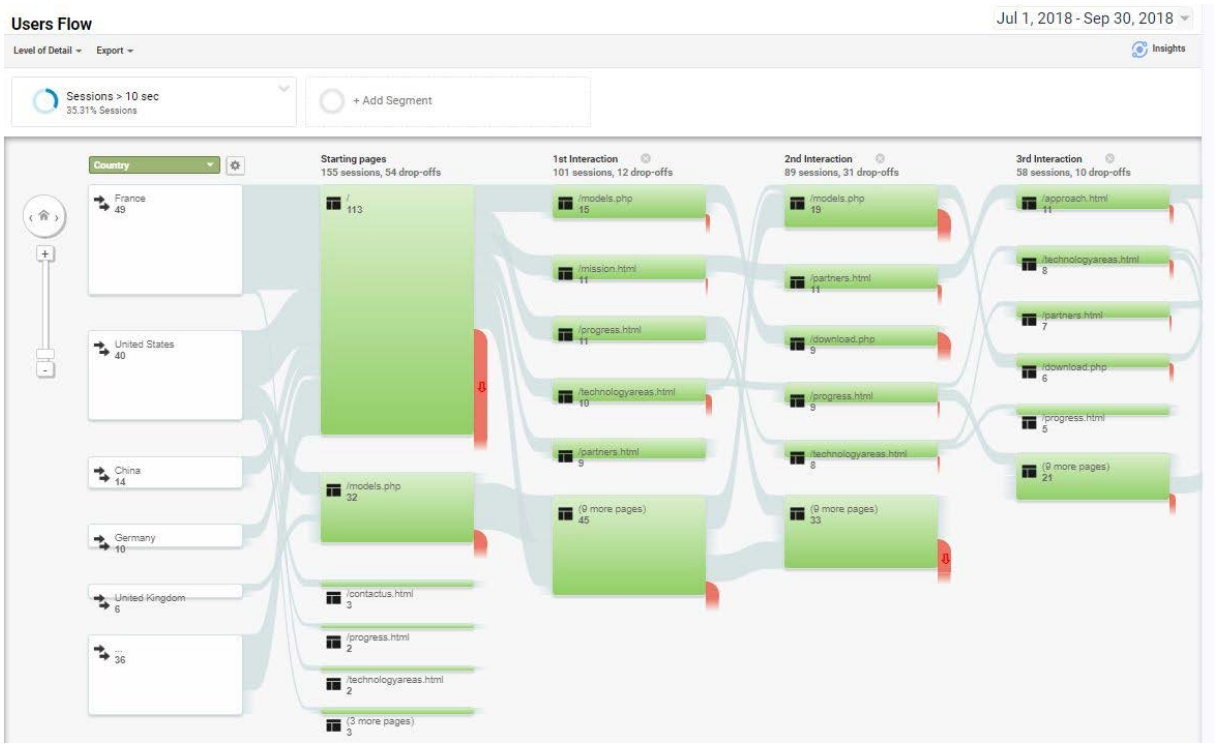

Figure 4. HSECoE web analytics: user flows

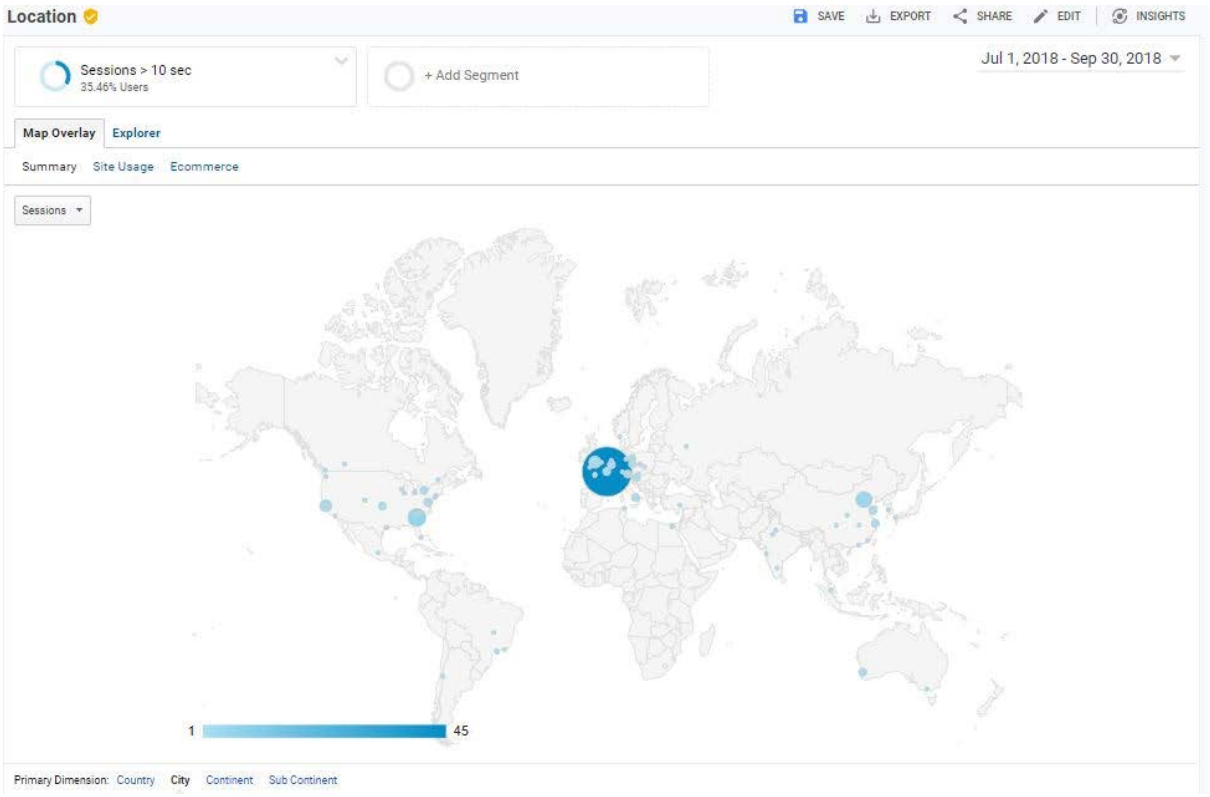

Figure 5. HSECoE web analytics: user origin countries

CONCLUSIONS AND UPCOMING ACTIVITIES

- Work with HSECoE partners to continue to update and improve models developed by the center; make these models available and accessible to the broader research and academic community through a controlled web-based access portal; and track downloads and website activity.
- Create stand-alone executable versions of the HSECoE-developed material storage models to provide first-order storage system estimates based on material property information.
- Update the hydrogen storage equations with additional, alternative theoretical storage system formulations to allow users to choose the most appropriate theory for their material.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. David A. Tamburello, Matthew R. Kesterson, and Bruce J. Hardy. "Heat Transfer Unit and Method for Prefrabricated Vessel." US patent 9,809,380 B2 (November 7, 2017).

FY 2018 PUBLICATIONS/PRESENTATIONS

1. D. Tamburello, M. Thornton, S. Sprik, and K. Brooks, "Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements," U.S. Department of Energy Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, June 15, 2018.
2. D. Tamburello, M. Thornton, S. Sprik, and K. Brooks, "Hydrogen Storage System Modeling Support: HSECoE System Modeling Update," Hydrogen Storage Technical Team Review, January 18, 2018.
3. Bruce Hardy, David Tamburello, and Claudio Corgnale, "Hydrogen Storage Adsorbent Systems Acceptability Envelope," International Journal of Hydrogen Energy 43, no. 42 (October 18, 2018): 19528–39, https://doi.org/10.1016/j.ijhydene.2018.08.140.

4. David Tamburello, Bruce Hardy, Martin Sulic, Matthew Kesterson, Claudio Corgnale, and Donald Anton, "Compact Cryo-Adsorbent Hydrogen Storage Systems for Fuel Cell Vehicles," Proceedings of the ASME 2018 Power Conference, Paper no. 51395 (2018): V001T06A025, https://doi.org/10.1115/POWER2018-7474.

5. Kriston P. Brooks, Samuel J. Sprik, David A. Tamburello, and Matthew J. Thornton, "Design Tool for Estimating Chemical Hydrogen Storage System Characteristics for Light-Duty Fuel Cell Vehicles." *International Journal of Hydrogen Energy* 43 (2018): 8846–8858, https://doi.org/10.1016/j.ijhydene.2018.03.090.