Emergency Hydrogen Refueler for Individual Consumer Fuel Cell Vehicles

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Project ID: ST140

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Overview

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Timeline

- Project Start Date: August 27, 2018
- Project End Date: August 26, 2020
- Percent Complete: 33%

Budget

- Total Project Budget: $999,934
  - Contractor Share: $0
  - Federal Share: $999,934
- Funds Spent: $333,311

Barriers Addressed

- 100% Reaction Conversion of LiH to H_2
- Passively Controlled H_2 Gas Evolution over 15 Minutes
- Reduced cost from $391 to $83

Partners

- US DOE: Project Sponsor and Funding
- Skyhaven: Technical R&D
- National Technology & Engineering Solutions of Sandia, LLC : Modeling

Relevance

- A common concern for fuel cell vehicle operators is running out of hydrogen fuel
  - Sparse hydrogen filling stations
  - Operators can experience range anxiety
  - This lessens the appeal of these vehicles hindering their commercialization
- To overcome this shortfall, the DOE is interested in developing emergency hydrogen refuelers
  - Similar in concept to keeping a can of gas in the trunk
  - Compact and lightweight H_2 storage unit that can be stored in the vehicle trunk
  - Can be safely and reliably operated by the driver

Value Proposition

- To meet this market need, a H_2 gas refueler is being developed
- Skyhaven's refueler product goals
  - Provide 0.75 kg (1.7 lb) of hydrogen fuel
  - Refill the vehicle within 15 minutes
  - Activate with water giving it a long storage lifetime
  - Mass of 10 kg (22.8 lb) that includes the activating water
  - Compact space of 11 liters (0.4 ft^3)
  - No moving parts helping to increase reliability
  - Material cost budget of $83 in low production volumes
- With this product, the average fuel cell vehicle will have a 50 mile range enabling the operator to reach a hydrogen refueling station

Refueler Innovation

- Store lithium hydride powder in a hermetically sealed vessel
- When this chemical hydride is exposed to water vapor, it releases hydrogen gas instantaneously
  - $LiH + H_2O \rightarrow H_2 + LiOH$
- Use a network of water conduits placed throughout a packed bed of lithium hydride to shuttle liquid water
  - Liquid water pervaporates through the conduits introducing water vapor to the LiH particles
- Potential to use hydrophilic micro-wick additives within the LiH to further disperse water to all LiH particles giving 100% reaction yield

Water Activation of LiH to Release H_2 Gas: Vapor Versus Liquid Feed

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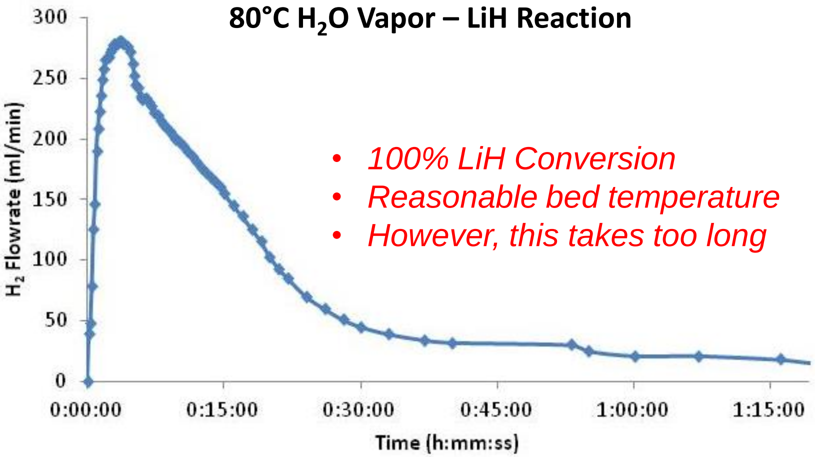
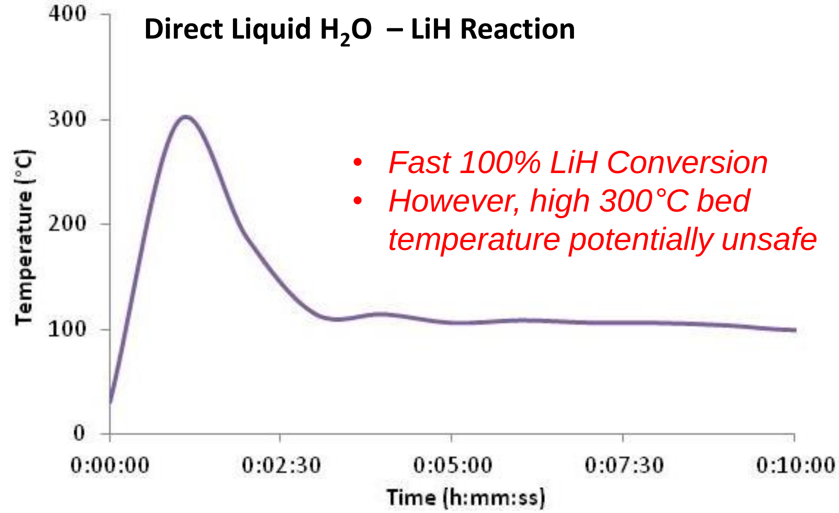
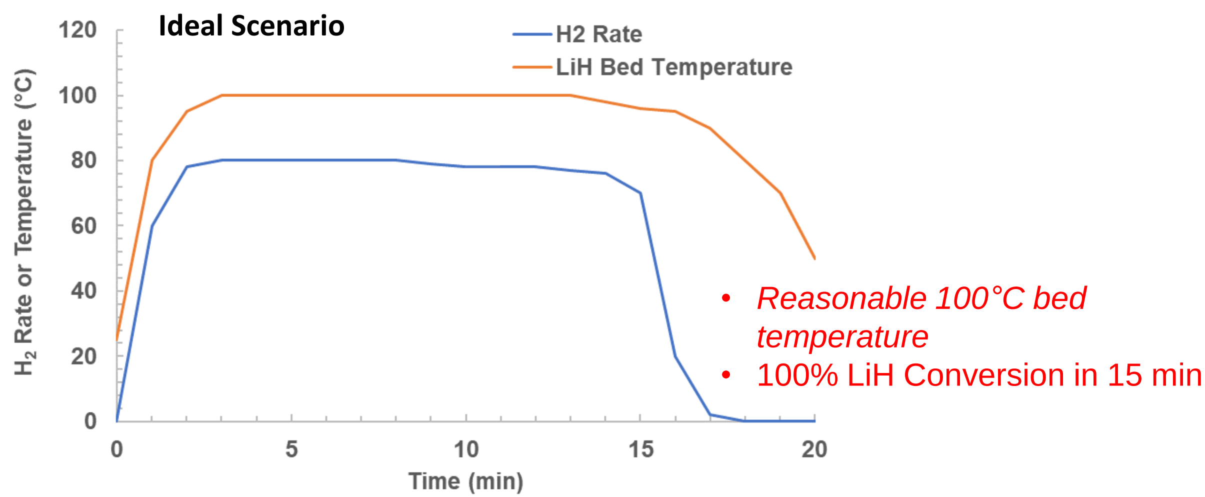
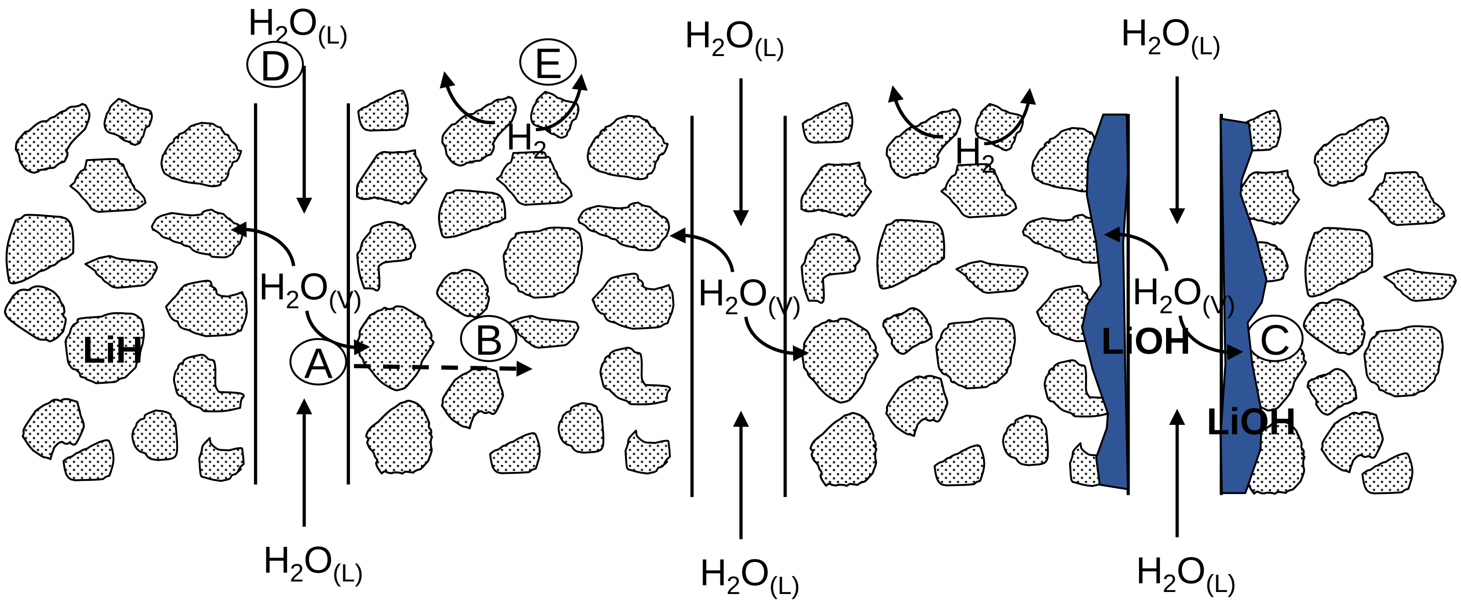




- Ideal scenario
  - React all LiH within 10-15 minutes
  - Maintain bed temperature less than 100°C using water vapor feed
  - Liquid water for bootstrapping



Refueler Technical Challenges



A : Maximizing the water vapor transport rate through conduit

B: Maximizing the distance that water vapor can transport into the LiH bed

C: Overcoming LiOH films that hinder water transport to LiH particles

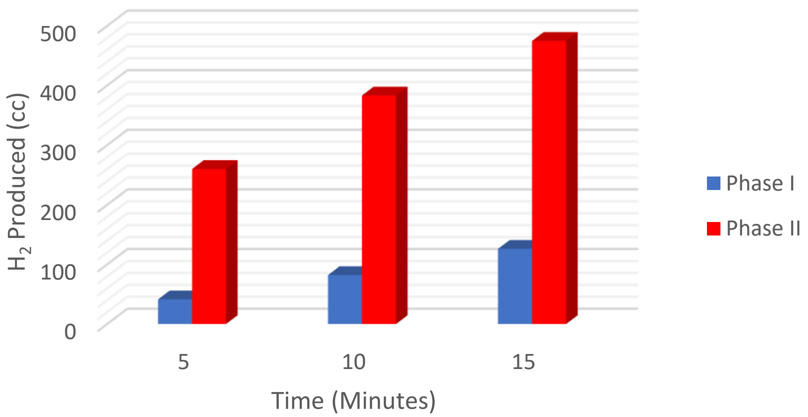
D: Introducing liquid water into the conduits without pumps

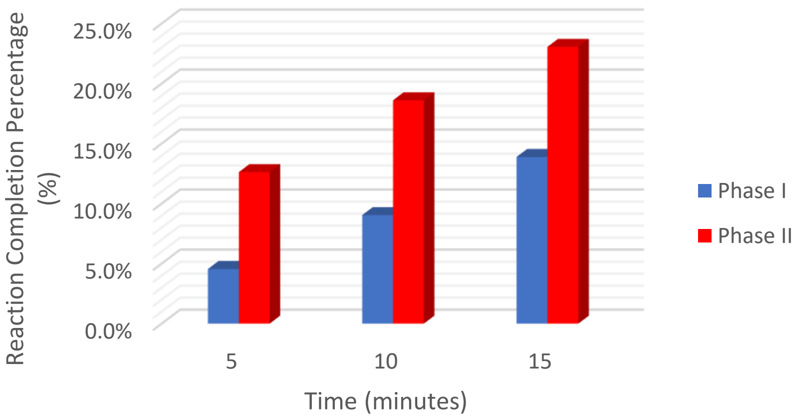
E: System engineering – start up, heat removal, H_2 purity, reliability, refueler design, cost

Single Conduit Refueler

- Single conduit (1.75” L, 1/8” OD) refueler performance using gravity feed water source
- Phase II refuelers fabricated without wick additives due to improved water vapor/liquid water permeation through the conduit
- Removal of wick additives in LiH bed minimize refueler size/cost while maximizing LiH content per unit volume

Water permeating through conduit

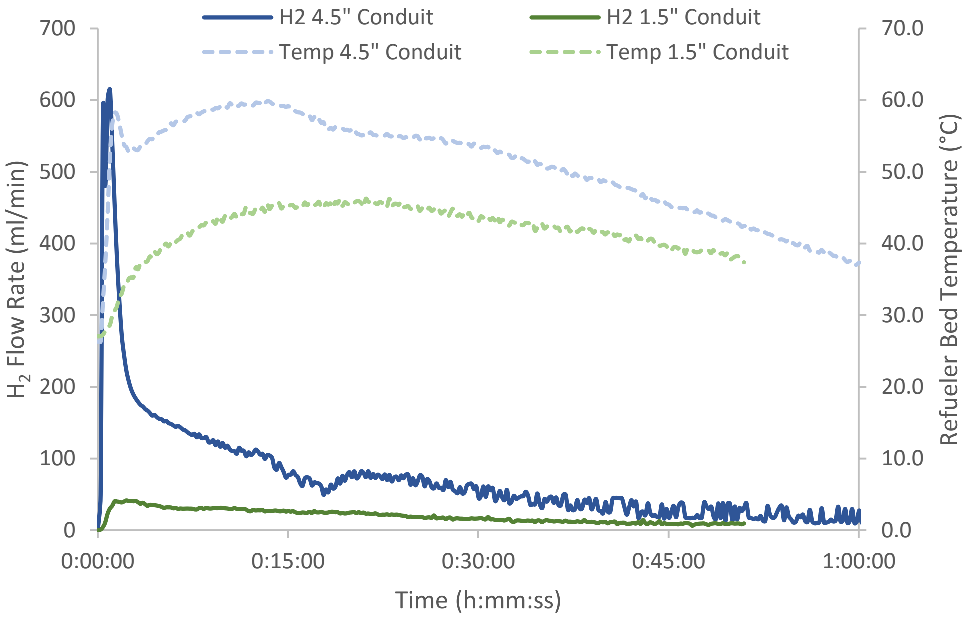




Phase I refueler data shown used 30% (wt) wick additives in LiH bed to improve water transport

Conduit Scaleup

- Increasing conduit length to 4.5” increases hydrogen flow rate greater than 3x over 1.5” length
- Heat from reaction provides higher refueler bed temperature which increases water vapor/liquid water permeation through conduit increasing hydrogen generation rate of refueler



HPC4Materials Program

- HPC4Materials program seeks qualified industry partners to participate in short-term, collaborative projects with the DOE's national laboratories
- Industry partners granted access to High Performance Computing (HPC) facilities and experienced staff at DOE National Laboratories
- Collaborative effort addresses key challenges in developing, modifying, and/or qualifying new or modified materials through the application of high performance computing, modeling, simulation, and data analysis
- The technical goal is to developed a robust multiphysics model of the refueler reactor that will be used to improve the design and performance of the current refueler prototype.
- Specifically, the following performance goal need to be achieved:
  - 100% LiH reaction conversion within 15 minutes
  - Maximum pressure inside the reactor bed below 2,000 psia
  - Temperature inside the reactor bed below 100 degrees Celsius
  - Reduce the reactor's mass and volume

CRADA Partnership

- Skyhaven will develop and conduct experimental measurements to ascertain physical and transport properties in LiH and LiH/LiOH mixtures including:
  - Thermal conductivities, water and hydrogen diffusivities, reaction rate expressions and reaction rate constants
- Sandia National Laboratories will develop and incorporate the physical and transport properties into a multiphysics model that solves the highly-coupled equations that describe the hydrogen generation process accounting for mass, energy, flow, and reaction rates
- Model will be developed in Aria, which is a Sandia National Laboratories in-house Galerkin finite element based program for solving coupled-PDE physics problems
- Aria is capable of solving nonlinear, implicit, transient state problems in 2D and 3D on parallel architectures

Determining the Reaction Rate

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- To determine reaction rate constants for LiH to H_2, small quantities of LiH or LiH/LiOH mixtures are reacted with a saturated gas stream
- Varied inlet gas saturation and reactor chamber temperature
- Looked at data for initial rate (where we assumed no LiOH diffusion issues).

$$R_{H2\,production} = k * [P_{H2O}]^m * [LiH]^n$$

  - P_{H2O}: in mm Hg, calculated with Antoine's equation at temperature of reactor
  - [LiH]: in mol, calculated at any given time by:

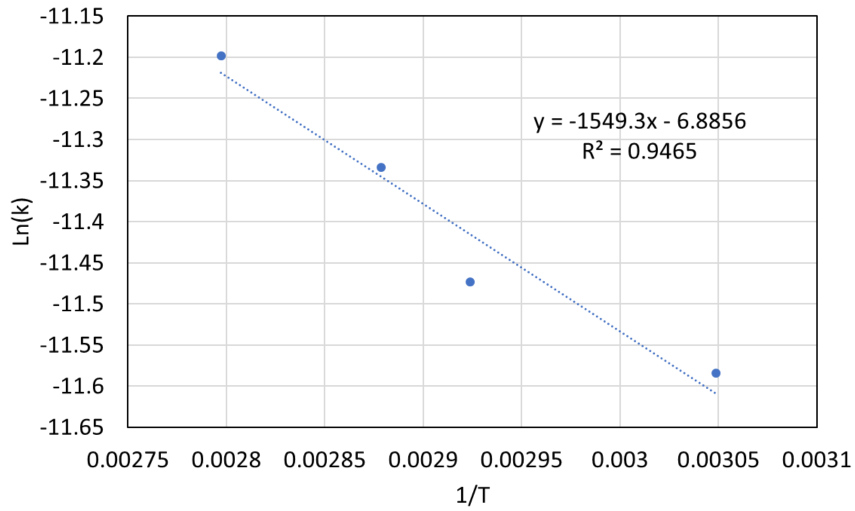
$$[LiH] = [LiH]_{in} - \frac{Vol_{H2}}{Molar\,Volume}$$

  - $R_{H2\,production}$ in mol/min
  - k = rate constant in $mmHg^{-1}\ min^{-1}$

Post run: LiH → LiOH

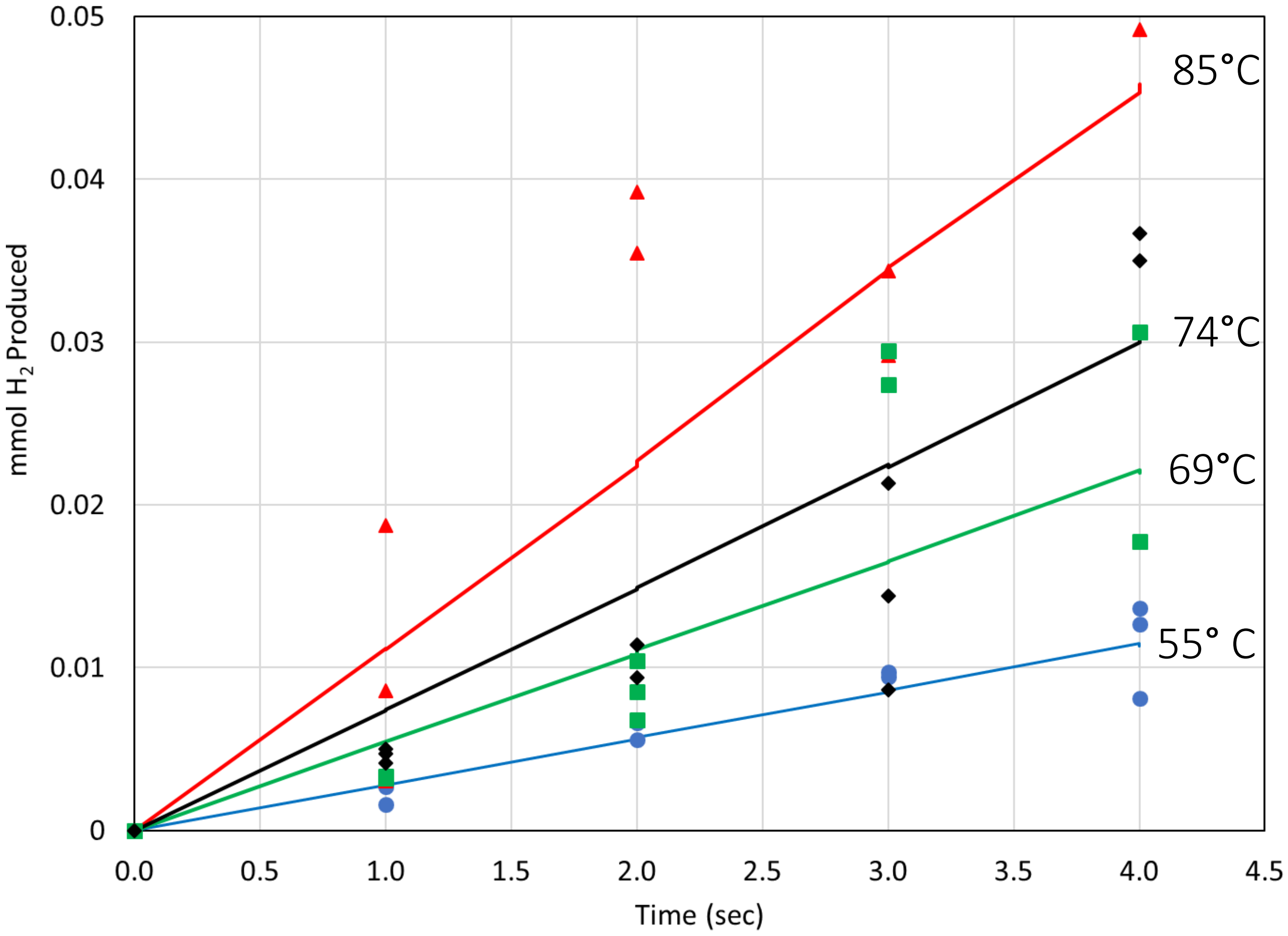
Data Regression

- Solved for four temperature data sets. Let k vary between four runs but made n and m equal for all four sets.
- Used $k = Ae^{\frac{-E_a}{RT}}$ to determine Ea
- Results depended on how much data was used (how long into the reaction)
- For 100% LiH testing $R_{H2\,production} = k * [P_{H2O}]^m * [LiH]^n$
  - n = 0.22, m = 0.82



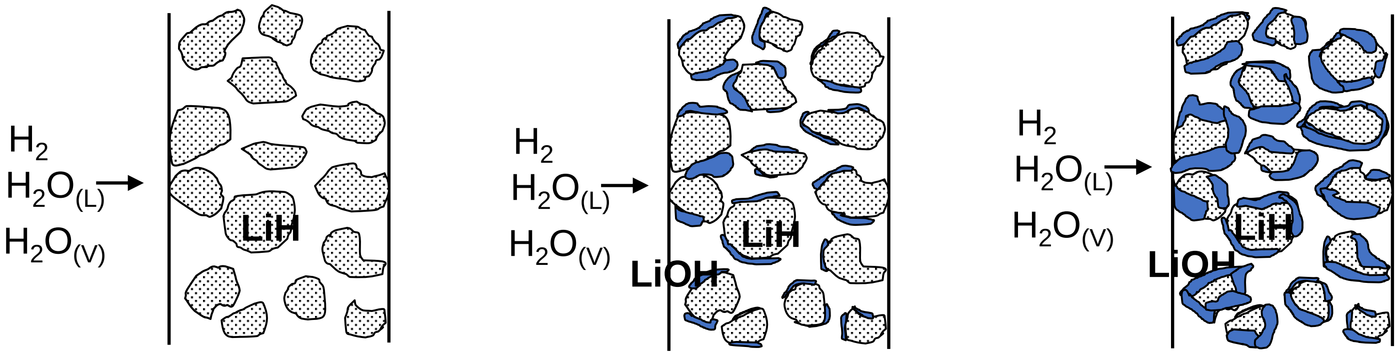
Temp (°C)	Temp (K)	k
55.0	328.0	9.32E-06
69.0	342.0	1.04E-05
74.4	347.4	1.20E-05
84.5	357.5	1.37E-05

Comparing Model to Data – 100% LiH



Diffusivity Measurement Objectives

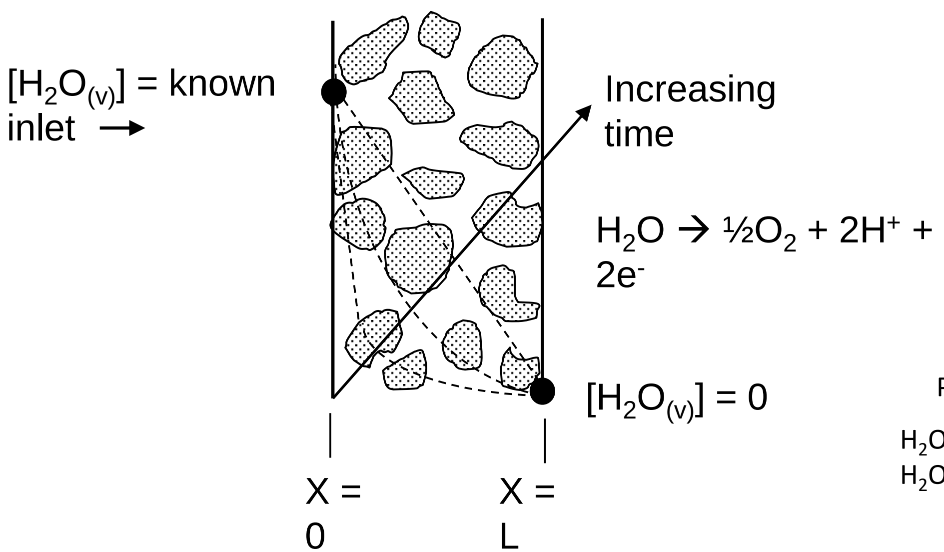
- Want to measure the diffusivity of $H_2O_{(v)}$, $H_2O_{(l)}$, and H_2 through packed beds with variables levels of LiH and LiOH

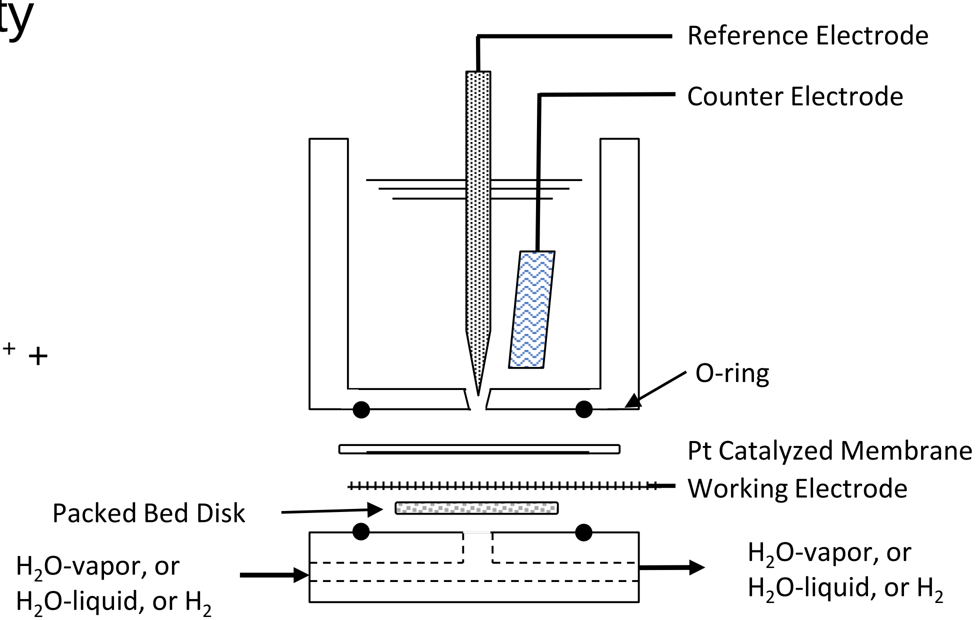


- Focus is on interparticle diffusivity within the packed bed, not intraparticle diffusivity
- Want a non-reactive compound similar to LiH compatible with water, hydrogen and LiOH with a comparable crystallinity and particle size as LiH
- Test approach on the suitability of a surrogate
  1) Diffuse H_2 with LiH/LiOH pellet – get $D_{H2,LiH}$
  2) Diffuse H_2 with salt/LiOH pellet – get $D_{H2, salt}$
  3) If $D_{H2, salt} = D_{H2,LiH}$ then surrogate okay to use with water diffusants

Use Electrochemical Monitoring Technique[1]

- Approach electrochemically oxidizes or reduces the diffusing molecule to a zero-concentration as it breaks through the packed bed
- Uses Fick's Law of Diffusion and the diffusion-limited current density to regress the diffusivity

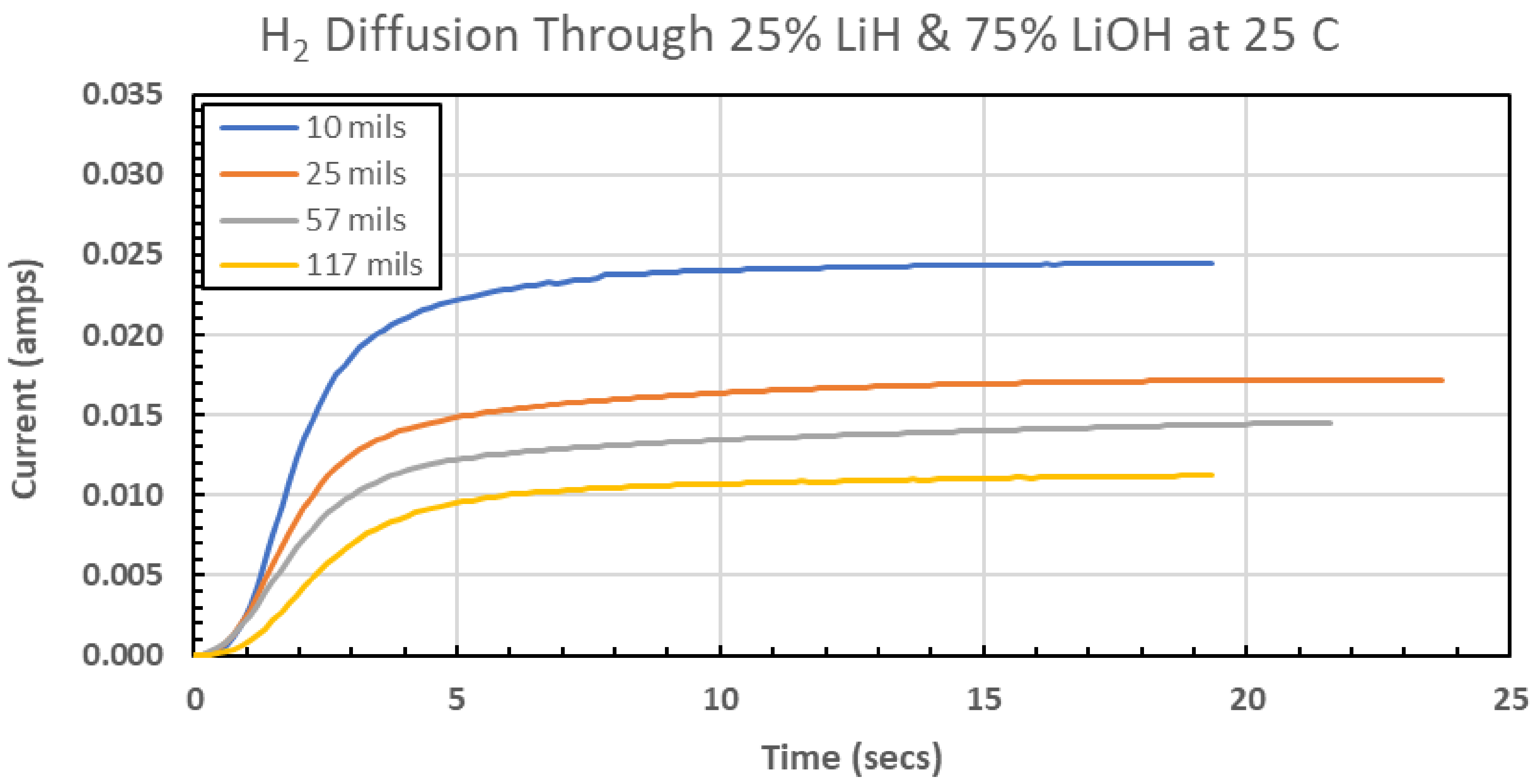




Experimental setup for measuring diffusion

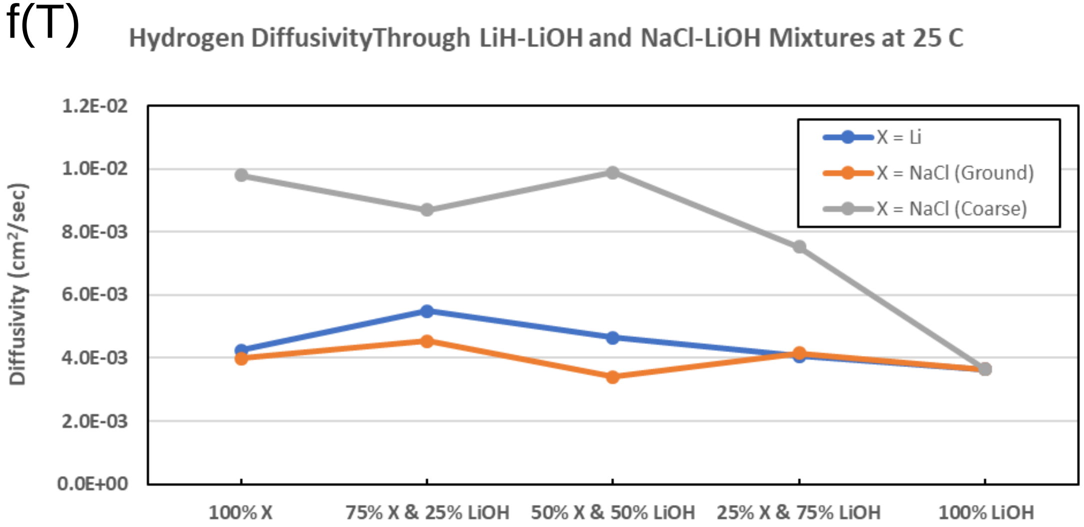
[1] M.C. Kimble, R.E. White, Y. Tsou, and R.N. Beaver, Estimation of the Diffusion Coefficient and Solubility for a Gas Diffusing Through a Membrane, *J. Electrochem. Soc.*, **137**, 2510 (1990).

Current Transient Response



H_2 Diffusivity Results

- Examined ground versus coarse salt as a surrogate for LiH
- Ground salt-LiOH mixtures show comparable diffusion behavior to LiH-LiOH mixtures
  - Ground salt is an acceptable surrogate for LiH
- Little variation in H_2 diffusivity coefficient for varying LiH-LiOH mixtures
  - $D(H_2) \sim f(T)$



Technology Status Today

- Phase I and II DOE programs have shown the technical feasibility of the hydrogen refueler
  - Demonstrated mechanisms to gravity feed water to the conduits
  - Showed conduits and operational methods that increase the water vapor transport rate through the conduits
  - Showed that only H_2 and water exit the refueler where a desiccant will adsorb the water before filling the fuel cell vehicle
  - Examined scale up using compartmented zones for heat removal and safe operation
- HPC4Materials program has developed test methodologies to measure reaction rate and diffusivity for use in Sandia's multiphysics model to describe the hydrogen generation process

H_2 Refueler Technology into the Future

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- DOE SBIR Phase II Program will be used to focus on further development of technology including:
  - Demonstrate the refueler meeting hydrogen safety standard J2719
  - Demonstrate the refueler operating up to 2000 psia
  - Show that the refueler can operate from sub-freezing to 40 °C environmental temperatures
  - Show that the refueler will dispense 750 g of hydrogen over a 15-minute refueling operation reacting 100% of the lithium hydride
  - Develop and integrate a water conduit network into a 3000 g lithium hydride packed bed to safely operate and control the hydrogen evolution reaction
  - Develop internal and external heat transfer cooling mechanisms to maintain the refueler outer surface temperature less than 100 °C
- HPC4Materials program will be used to further develop a robust multiphysics model of the refueler reactor that will be used to improve the design and performance of the refueler