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System Development for Vehicular Natural Gas Storage Using Advanced Porous Materials

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Public Executive Summary

This report is to provide a statement on the objectives, progress, and milestones of the research conducted to develop innovative advanced porous materials for the storage of natural gas for vehicular applications. These innovative porous materials will significantly increase the feasibility of natural gas fueled vehicles by decreasing costs associated with the storage and filling of natural gas tanks through enhanced packing of gas molecules within micropores. The adsorption of natural gas will be substantially increased by designing materials that optimally pack methane (the primary component of natural gas) and reduce unusable (dead) space within the structure. This was accomplished through a multi-organizational and multi-disciplinary effort that includes computational studies, laboratory-scale synthesis, scale-up and cost-reduction, and thorough characterization.

Acknowledgement

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Accomplishments and Milestones Update

The focus of the project was on building a commercially viable, high performance sorbent for the use of absorbed natural gas vehicles. Under the MOVE project, several new promising sorbents were developed. Our team has predicted the simulated capacity of over 15,000 structure; however, no sorbent has met the ARPA-E target. Using the computational models to guide our synthesis, a new route was developed to synthesize ultra-stable metal-organic frameworks (MOFs). Over forty new iron MOFs (Fe-MOFs) were synthesized with BET surface area over 2,000 m^2/g. Our new approach resulted in Fe-MOFs with enhanced methane loading capacity and stability while approaching the lucrative 10$/kg cost target. Although the performance target seems out of reach based on computational studies; we have synthesized gram scale quantities of PCN-250 (PCN stands for porous coordination network), a Fe-MOF with deliverable capacity that exceed other simulated materials. Additionally, great strides have been made in MOF scale-up (~50/kg, PCN-250) and densification (>80% volumetric and gravimetric working capacity, PCN-250). A number of tasks and milestones were laid out in Attachment 3, the Technical Milestones and Deliverables, at the beginning of the project. The actual performance against the stated milestones is summarized below:

Table 1. Key Milestones and Deliverables.

Task	**Accomplishments**
Task 1 – Sorbent Development	
1.1 Modeling	
1.1.1 Computational models for Gen1 sorbents developed	Computational models have been developed based on several previously synthesized porous polymer networks (PPNs). The models have led to a better understanding of experimental findings, and can therefore lead to design of improved materials for vehicular methane storage
1.1.2 Predictive model sorbent bulk properties completed	A model that predicts sorbent bulk properties has been created by LBNL and has been used to predict the deliverable capacities of ~15000 structures.
1.1.3 Library of sorbents and bulk properties delivered	We have concluded that our list of materials with working capacity greater than the above-stated target consists of zero materials.

1.2 **Synthesis**	
1.2.1 New Gen1 sorbents synthesized	Five Zr-MOFs and eight Fe-MOFs having a BET surface area over 2000 m^2/g have been synthesized.
1.2.2 New Gen2 sorbents synthesized	More than 40 stable Fe-MOFs with promising methane uptake have been obtained in gram scale through a new synthetic pathway from cheap starting materials.
1.3 Characterization	
1.3.1 Gen0 materials characterization completed	Characterization of Gen0 materials has been completed. Adsorption measurements with CH_4 and pipeline gas have been conducted to measure deliverable capacity between 35 and 5.8 bar, and between 65 and 5.8 bar.
1.3.2 Gen1 materials characterization completed	Excess methane adsorption isotherms for Gen1 materials have been obtained at 298K.
1.3.3 Go/No-Go: Record performance sorbent achieved	PCN-62 has been shown to have surpassed the target of 125% of PCN-14, having achieved uptake as high as 220 $cm^3 \cdot cm^{-3}$.
1.3.4 Gen2 materials characterization completed	Methane and pipeline gas uptake has been measured for three Gen2 Fe-MOFs and show improvements in chemical stability in comparison to Gen1 materials.
1.3.5 Go/No-Go: Record performance sorbent achieved	Synthesis of record performance sorbent was not achieved. Simulation studies by LBNL have shown that no candidate MOF exist that exceed the current methane target. However, several robust MOFs have been synthesis.
In Task 2 – Scale-up	
2.1 Scale-up synthesis	
2.1.1 Bulk-scale quantity of Gen0 delivered	We have scaled up the synthesis of PPN-4 by 2, 4, 8, 16, and 32 times the literature preparation.

2.1.2 Bulk-scale quantity of Gen1 delivered	The project team has produced 1.3 kg of Gen1 MOF (PCN-62), through bench-scale synthesis, with the product exhibiting similar physical properties and preparation yields as experienced in much smaller lab-scale preparations.
2.1.3 Bulk-scale quantity of Gen2 delivered	RTI successfully prepared a large batch (> 48 g) of ligand needed to prepare PCN 250'. Using this ligand RTI then prepared > 4g of the bi-metallic MOF. RTI has also successfully prepared more than 20 g of the Fe-based PCN 250.
2.2 Synthesis cost-reduction analysis	
2.2.1 Low-cost synthesis pathways identified for Gen0 materials	Low cost synthesis pathways for Gen0 (PPN-4) have been identified and sorbent materials prepared by these low cost synthesis routes.
2.2.2 Cost analysis of Gen1 synthesis completed	Cost analysis for lab-scale Gen1 candidate sorbent, PCN-70, has been performed and exhibits an order-of-magnitude cost reduction relative to Gen0 PPN-4. The cost of this particular sorbent remains too high for ANG vehicle application, but more recent discoveries of Fe-based MOFs show greater potential to meet a $10/kg sorbent cost target.
2.2.3 Cost analysis of Gen2 synthesis completed	The project team has completed a cost analysis for Gen2 (Fe-based PC-250) materials synthesis. Using a previously developed cost model, it is estimated that this MOF can be prepared for a cost of about $50/kg.
2.2.4 Cost methodology completed	The cost methodology for screening ANG sorbent candidates has been completed. The cost methodology has been applied to all sorbent developed and considered on this project.

Task 3 – Bulk testing	
3.1 Densification strategies	
3.1.1 Identify methods for densification, forming, and physical property enhancement	We have identified two approaches for pelletizing PPN-4: the first is a mechanical-based approach, where PPN-4 powder would be pressed, with or without a binder, into a pellet
3.1.2 Gen0 densified pellets fabricated	Densified pellet forms of Gen0 (PPN-4) sorbents have been fabricated and characterized and exhibit a surface area of 3,840 m^2/g (5% lower than the PPN-4 powder) with an average crush strength measured as high as 0.5 N/mm.
3.1.3 Gen1 densified pellets fabricated	The project team has fabricated structured pellets from Gen1 (PCN-62) sorbent materials. Three Gen1 pellet samples (produced from various techniques) achieve >80% retention of surface area compared to Gen1 powdered forms.
3.2 Pellet scale testing	
3.2.1 Go/No-Go: Gen0 pellet performance characterized	Densified (pelletized) Gen0 (PPN-4) sorbents have been fabricated and characterized and exhibit higher gravimetric and volumetric methane uptake compared to PPN-4 powder. Total volumetric adsorption is about 85 $cm^3 \cdot cm^{-3}$ at 50 bar compared to 65 $cm^3 \cdot cm^{-3}$ for the powder.
3.2.2 Go/No-Go: Gen1 pellet performance characterized	The excess gravimetric methane uptake of the PCN-250 powder from TAMU is slightly higher but comparable to large scale Gen2 material from RTI.
Task 4 – Technology to market strategy	
4.0.1 Revised T2M Plan submitted, IP agreements signed	T2M Plan has been submitted and IP agreements have been signed.
4.0.2 Material manufacturer initial engagement made	Initial engagements with commercial material manufacturers have been made.. Albermarle's Fine Chemicals R&D Department has been identified as the entity

	with the greatest potential for fruitful partnership.
4.0.3 Initial cost model developed	A framework for an initial sorbent cost model has been developed.
4.0.4 Preliminary market opportunity for both ANG and early adopters completed	A preliminary market opportunity analysis for both ANG and early adopters is complete. Gas cylinder replacement and vehicular use represent very large, long-term markets with different needs and different incumbent technologies.
4.0.5 Revised T2M Plan Completed	The project team's technology-to-market (T2M) plan has been updated to include information on the market opportunity analysis and value propositions for various ANG sorbent markets.
4.0.6 Initial cost-down plan completed, options for next stage funding identified	The project team has conducted a preliminary review of next stage funding options. Additionally, the team has identified the major MOF production areas that require improvement and will have the greatest impact on decreasing manufacturing costs towards the $10/kg ARPA-E MOVE Program product cost target.
4.0.7 Tier 2 manufacturers engaged; Revised T2M plan completed	Potential future partners and manufacturers of the MOF-based sorbents have been engaged (Strem chemicals and Albemarle Fine Chemicals).
4.0.8 Cost-down plan refined; Next stage funding secured	No significant next stage funding opportunities (multi-million dollar, multi-year projects) have been identified and secured. RTI International has put together an internal business case for their management to consider for allocation of strategic investment funds to pursue a spin-off company focused on MOF scale-up.

Project Activities

The focus of our project was to synthesize a record breaking sorbent with comparable energy density to compressed natural gas. Our multi-organization team used the strength the partners to address the many technical issue of our project. Computational modeling was performed by LBNL to understand the molecular interaction within the framework that improve methane uptake capacities. The bench scale synthesis of new MOFs based on the computational models was performed by TAMU. The new materials produced by TAMU were further characterized for high pressure methane loading by GM, with the best performing materials studied for scale-up and densification by RTI. Upon completion of this project, PCN-250 was synthesized with an excess methane capacity of 220V/V and a scale-up cost of ~50$/kg. Although PCN-250 is an outlier among simulated porous materials, the performance does not exceed the ARAP-E target.

Project Outputs

A. Journal Articles

B. Papers

1. Chen, Y.-P.; Liu, Y.; Liu, D.; Bosch, M.; Zhou, H.-C., "Direct Measurement of Adsorbed Gas Redistribution in Metal-Organic Frameworks." *J. Am. Chem. Soc.*, **2015**, 137, 2919-2930

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3. Zou, L.; Feng, D.; Liu, T.-F.; Chen, Y.-P.; Fordham, S.; Yuan, S.; Tian, J.; Zhou, H.-C., "Facile One-pot Synthesis of Porphyrin Based Porous Polymer Networks (PPNs) as Biomimetic Catalysts." *Chem. Commun.* 2015, 51 (19), 4005-4008.

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7. Liu, T.-F.; Feng, D.; Chen, Y.-P.; Zou, L.; Bosch, M.; Yuan, S.; Wei, Z.; Fordham, S.; Wang, K.; Zhou. H.-C., "Topology Guided Design and Syntheses of Highly Stable Mesoporous Porphyrinic Zirconium MOFs with High Surface Area." *J. Am. Chem. Soc.*, 2015, 137, 413–419.

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11. Kizzie, A. C.; Dailly, A.; Perry, L.; Lail, M. A.; Lu, W.; Nelson, T. O.; Cai, M.; Zhou, H.-C.,"Enhanced Methane Sorption in Densified Forms of a Porous Polymer Network." *Materials Sciences and Applications*, 2014, 5, 387-394.

12. Zhang, M.; Bosch M.; Gentle, T.; Zhou, H.-C., "Rational Design of Metal-Organic Frameworks with Anticipated Porosities and Functionalities." *CrystEngComm.* 2014, 16, 4069-4083.

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14. Zhang, M.; Chen, Y.-P.; Bosch, M.; Gentle, T.; Wang, K.; Feng, D.; Wang, Z. U.; Zhou, H.-C., "Symmetry-Guided Synthesis of Highly Porous Metal-Organic Frameworks with Fluorite Topology." *Angew. Chem. Int. Ed.*, 2014, 53, 815-818.

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C. Status Reports

D. Media Reports

E. Invention Disclosures

F. Patent Applications

G. Licensed Technologies

H. Networks/Collaborations Fostered

I. Websites Featuring Project Work Results

J. Other Products (e.g. Databases, Physical Collections, Audio/Video, Software, Models, Educational Aids or Curricula, Equipment or Instruments)

K. Awards, Prizes, and Recognition

Follow-On Funding

No significant next stage funding opportunities (multi-million dollar, multi-year projects) have been identified and secured. RTI International has put together an internal business case for their management to consider for allocation of strategic investment funds to pursue a spin-off company focused on MOF scale-up.