Experimental Characterization of Adsorption and Transport Properties for Advanced Thermo-Adsorptive Batteries

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Abstract

Thermal energy storage has received significant interest for delivering heating and cooling in
both transportation and building sectors. It can minimize the use of on-board electric batteries for
heating, ventilation and air-conditioning (HVAC) in electric vehicles (EVs) or reduce electricity
consumption during peak demand in residential and commercial buildings. A compact and light-
weight advanced thermo-adsorptive battery (ATB) is currently being developed to provide both
heating and cooling. Additionally, if waste heat or solar energy were used to regenerate the ATB,
the mechanical energy to run the cycle for vapor compression and transport, can be eliminated,
thus, providing a significant benefit over conventional HVAC systems, especially when
provision of electric energy is challenging.

We present a detailed characterization of the thermophysical and transport properties of
adsorptive materials for the development of the ATB. We discuss the feasibility of using
contemporary adsorptive materials, such as zeolite 13X, by carrying out a detailed experimental
and theoretical characterization. Enthalpy of desorption of zeolite 13X – water pair was
characterized using the state of the art calorimetric technique. The experimental characterization
and theoretical modeling of commercially available zeolite 13X (Sigma Aldrich, molecular sieves, 13X, powder, ~2 μm average size) combined with carbon nano-materials, such as functionalized multi-walled carbon nanotube and graphene, are carried out to improve the effective thermal conductivity. Furthermore, we carried out performance characterization of a single-layer adsorption stack for the development of the ATB. Consequently, this thesis can serve as a framework for the development and characterization of adsorption-based thermal storage systems.

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1. Introduction

1.1 Motivation

State-of-the-art energy storage systems are mainly based on electrochemical technology [1]. However, more than 90 % of the generated energy world-wide is consumed and wasted thermally [2]. In 2010, the U.S. energy consumption represented 19 % of the global energy consumption, 41 % of which was consumed by the building sector and 29 % by the transportation sector [3]. Half of the energy consumption in the building sector is used by space heating (37 %), cooling (10 %), and ventilation (3 %). In addition to the thermal energy needs for buildings, the rapidly growing electric vehicle (EV) industry requires substantial amount of energy in the form of heat. From 2010 to 2012, the plug-in EV sales in the U.S. increased 177 times [4]. However, EV technology faces a substantial challenge in terms of driving range, especially when the EV’s climate control relies completely on the onboard electric battery, which can reduce the driving range up to 40 % [5]. For cooling in an EV cabin, the automotive vapor compression cycle provides a coefficient of performance (COP) typically between 1.6-2.2 [6]. For heating, resistive heaters (e.g., PTC heaters) provide a COP never exceeding 1. There are substantial energy needs in the form of heat, and therefore, adsorption-based thermal storage systems have received significant attention due to recent advances in adsorptive materials with extremely high adsorption capacity [7-12]. Adsorption-based heat-driven cycles offer potential benefits over the conventional work-driven cycles (e.g., vapor compression cycle), by providing less systematic complexity and eco-friendly perspectives. If waste heat or solar energy were used to drive the adsorption cycle, the mechanical energy required to run the cycle via electricity or gasoline can be significantly reduced [13-17]. Additionally, adsorbents utilizing water as an adsorbate promise energy-dense heat storage systems providing both heating and cooling due to
water's high heat of phase change and enthalpy of adsorption [18-20]. However, thermophysical and transport characterizations of these materials are not well established, leading to underutilization of advanced materials, such as modified zeolites and Metal Organic Frameworks (MOFs).

1.2 Background

Research over the past few decades on adsorption-based cooling and heating systems has revealed significant potential for adsorption-based heating, ventilation and air-conditioning (HVAC) systems. High-surface-area zeolites [7, 8] and, more recently, metal-organic frameworks (MOFs) [9-12] hold the promise of replacing current HVAC systems with high-energy-density adsorption-based systems. A thermodynamic cycle representing an adsorption-based heat pump is shown in Figure 1, where $T_{evap}$, $P_{evap}$, $T_{cond}$, and $P_{cond}$ are the evaporator temperature and pressure, and condenser temperature and pressure, respectively. During the system operation, the temperature of the adsorbent varies between $T_a$ and $T_d$ (e.g., 60 to $100 \, ^\circ C$) and the pressure is set by the evaporator saturation temperature, unless there is a large pressure drop between the adsorbent and evaporator. During the system regeneration, the temperature of the adsorbent varies between $T_b$ and $T_c$ (e.g., 150 to $350 \, ^\circ C$) and the pressure is set by the condenser saturation temperature. $Q_{evap}$ denotes the heat input to the evaporator during the operation, and $Q_{cond}$ is the heat output from the condenser during the regeneration process. $Q_{adsorb}$ is the heat released via adsorption process, and $Q_{desorb}$ is the heat input into the adsorbent during the regeneration process. If waste heat or solar energy is utilized to regenerate the adsorption-based systems, the mechanical energy required for energy regeneration, $Q_{desorb}$, will reduce significantly and therefore, could replace the conventional HVAC systems [13-17].
However, due to their large micro-pore volume and the thermally non-conductive properties, adsorbents, such as ceramics like zeolites and organic materials like MOFs, have poor thermal transport characteristics, which severely limits their adsorption capacities [21, 22]. In addition to their poor thermal transport characteristics, zeolites and MOFs also provide relatively slow vapor transport rates when densified in the form of a stack to increase the volumetric energy density by reducing their composite porosity [23]. Furthermore, experimental characterization of energy associated with adsorption and desorption processes are still not well understood. In order to address these limitations, it is indeed necessary to provide a framework for the development and characterization of the adsorption-based thermal storage systems.

![Thermodynamic cycle of adsorption heat pump.](image)

**Figure 1 - Thermodynamic cycle of adsorption heat pump.**

### 1.3 Description of System

The ATB aims to provide cooling and heating capacities of 2.5kWh with 30 L of volume and 35 kg of total weight. The high enthalpy of vaporization of water, 2256 kJ/kg, high enthalpy of adsorption of water (typically 1.5 times higher than the enthalpy of evaporation with zeolites
[18-20]), and an innovative system design (a monolithic integration strategy, see Figure 2) make it possible to create a compact and light-weight thermal storage system. Operational components of the ATB are the adsorbate reservoir, evaporator, condenser, and adsorption bed. During the ATB operation, liquid adsorbate is supplied through an expansion valve from the reservoir and evaporates on the evaporator at ~ 3 °C. Spontaneous vapor adsorption at ~ 760 Pa vapor pressure in the adsorption bed then releases heat. During summer, cooling is provided by the evaporator, and during winter, heating is provided by the adsorption bed. During regeneration, the adsorption bed is heated up to 150-350 °C, causing desorption. Desorbed vapor is then condensed on the condenser surface and subsequently collected in the reservoir for the next operational cycle. The ATB operation during adsorption and regeneration is shown in Figure 3 and Figure 4, respectively. If one needs to consider freezing point suppression of water, methanol can be added as an anti-freeze, which provides a relatively high enthalpy of vaporization, 1104 kJ/kg, while lowering the freezing point by 5-20 °C with a fraction of 15-25 % [24].

The strategy for the monolithic integration of the cold side (evaporator) and hot side (adsorption bed) of the ATB [25, 26], as illustrated in Figure 2, reduces the system volume and weight by combining the evaporator and condenser units. Increased interface area between the evaporator/condenser unit and the adsorption bed by interfacing the evaporator/condenser next to the adsorption bed enhances the mass transport rate of vapor phase significantly. After water evaporates from the evaporator, the vapor immediately transports through the gaps between adsorption stacks, ~ 200 μm, followed by adsorption within the stack. The coolant loop interfaced with the adsorption bed dissipates the heat released during the adsorption process. During the regeneration, the adsorption bed is heated with an attached electric heater (150 – 350 °C) causing desorption, and desorbed vapor condenses on the condenser (The same heat
exchanger can be used for the evaporator. Condensed liquid is then sent back to the reservoir for the next operational cycle.

Figure 2 - Design of monolithically integrated adsorption system. Complete system requires hermetically sealed housing with coolant loops. Adsorbate reservoir is not included in image.
Figure 3 – ATB operational diagrams of cooling and heating modes. For cooling mode, cooling is provided by evaporator and adsorbent dissipates heat to ambient. For heating mode, heating is provided by adsorbent and evaporator is heated by ambient.

Figure 4 – ATB operational diagram of regeneration. For regeneration, adsorbent is heated by heater and adsorbate condenses on condenser. Condenser dissipates heat to ambient and collected liquid phase adsorbate send back to reservoir.
1.4 Theoretical Analysis of Vapor and Thermal Transport

Transport processes during adsorption are governed by three coupled equations [23, 27-29]: mass conservation, energy conservation, and adsorption dynamics, shown in Equations (1), (2), and (3), respectively.

\[
\varepsilon \frac{\partial C}{\partial t} + \nabla (u \cdot C) = \nabla \cdot (\varepsilon D_v \nabla C) - (1 - \varepsilon) \frac{\partial C_\mu}{\partial t} \quad (1)
\]

\[
\langle \rho c_p \rangle \frac{\partial T}{\partial t} + \langle \rho c_p \rangle u \cdot \nabla T = \nabla \cdot (k) \nabla T + h_{ad} (1 - \varepsilon) \frac{\partial C_\mu}{\partial t} \quad (2)
\]

\[
\frac{\partial C_\mu}{\partial t} = \frac{1}{v} \int D_\mu \cdot \nabla C_\mu \cdot \mathbf{n} \, dA. \quad (3)
\]

In Equation (1), \( C \) is the concentration of the vapor phase, \( C_\mu \) is the concentration of the adsorbed vapor within the adsorption bed, \( D_v \) is the intracrystalline diffusivity, and \( \varepsilon \) is the porosity of the bed. \( u \) is the Darcian velocity of the vapor phase, which is calculated using the following equation

\[
u = -\frac{K}{\mu_v} \nabla P, \quad (4)
\]

where \( K \) is the permeability of the adsorption bed, which is given by

\[
K = \frac{2 \pi^2 \cdot \varepsilon^3}{75 \cdot (1 - \varepsilon)^2}, \quad (5)
\]

where \( r_c \) is the crystal radius of adsorbent [30].

In Equation (2), \( h_{ad} \) is the enthalpy of adsorption, \( \langle k \rangle \) is the volumetrically averaged thermal conductivity of the adsorption bed, and the average specific heat, \( \langle \rho c_p \rangle \), can be represented using the mixture rule,

\[
\langle \rho c_p \rangle = (1 - \varepsilon) \rho_c c_{p,c} + (1 - \varepsilon) MC_\mu c_{p,\mu} + \varepsilon MC c_{p,v}, \quad (6)
\]

where \( \rho_c \) is the crystal density of the adsorbent and \( c_{p,c} \) is the specific heat of the dehydrated adsorbent. \( M, c_{p,\mu}, \) and \( c_{p,v} \) are the molecular weights of the adsorbate, the specific heat of the
adsorbed phase, and the specific heat of vapor phase, respectively. To illustrate the importance of
the adsorbent thermal conductivity, a simple system was modeled, as shown in Figure 5 [23].
The thermal conductivity of the adsorbent was varied from 0.5 to 5 W/mK and the volumetric
adsorption rate was calculated as shown in Figure 6. As the thermal conductivity of the adsorbent
increases, the adsorbent composite dissipates heat faster, lowering the operational temperature of
the adsorbent. And as a result, this process increases the volumetric adsorption rate because of
the higher equilibrium uptake capacity with reduced temperature and greater relative pressure.

Figure 5 - Schematic diagram of coaxial adsorption bed with coolant pipe. Ri = 5 mm, Ro = 20
mm, and Tcoolant = 300 K.
Figure 6 - Simulated volumetric adsorption rate vs. time with various thermal conductivities, \( k \), of system illustrated in Figure 5.

1.5 Overall Objectives and Thesis Outline

The objective of this thesis is focused on the experimental characterization of adsorption and transport processes using the contemporary adsorptive material zeolite 13X (ZT). Chapter 1 introduces the motivation, background, description of the ATB system, and fundamental transport processes during adsorption. In Chapter 2, we carry out systematic characterizations of the adsorptive material, ZT, using various experimental techniques. In Chapter 3, we present
experimental characterization of adsorption stack. In Chapter 4, we present conclusions and suggest future work.
2. Systematic Characterization of Zeolite 13X

In this chapter, we report a detailed material thermophysical and transport characterization of zeolite 13X (ZT) [31]. Experimental characterization includes determination of porosity and crystal density of adsorbent, adsorption and desorption kinetics, enthalpy of adsorption and desorption, and thermal transport of composite materials made of ZT and carbon nano-materials.

2.1 Experimental Characterization of Average Porosity, Crystal Density, and Permeability of Adsorption Bed

Experimental characterization of porosity and its effect on the overall heat and mass transport phenomena using the adsorbent is an important step towards optimization of adsorption systems [23]. The experiment used to determine porosity of ZT composite were also used to confirm the reported crystal density of ZT [32], 1470 kg/m$^3$, using the following relation between porosity and crystal density, shown in Equation (7):

$$ \rho_{\text{bed}} = \rho_{\text{crystal}} \cdot (1 - \varepsilon) $$  \hspace{1cm} \text{(7)}

where $\rho_{\text{bed}}$ denotes the density of the adsorption bed and $\rho_{\text{crystal}}$ is the crystal density of the adsorbent.

A simple experimental set-up, shown in Figure 7, composed of a high pressure gas tank connected to a flow meter and a pressure sensor was used to measure the porosity and the crystal density of a sample fabricated by packing the adsorbent into a cylinder. The Kozeny-Carman relation [33] for porous media, shown in Equation (8), was used to determine the porosity as a function of the dehydrated adsorbent density, as shown in Figure 8:
In Equation (8), \( \frac{\Delta P}{L} \) is the pressure drop across the packed sample in Pa, \( L \) is the length of the packed sample in m, \( u \) is the flow velocity in m/sec, \( \mu \) is the gas viscosity in Pa·sec, \( \epsilon \) is the porosity of the sample, \( \varphi \) is the sphericity of the sample, and \( d_p \) is the particle diameter of the sample in m. Sphericity was found to be 0.846, assuming ZT to be an octahedron crystal [34]. The nominal particle diameter of ZT crystals, as indicated by the manufacturer, is \(~2\mu m\). Based on the porosity measurements, the crystal density of ZT was determined to be 1534.9 kg/m\(^3\) from Equation (7), which is within 4.5% of the reported crystal density of ZT, 1470 kg/m\(^3\) [32]. It is important to note that Equations (7) and (8) may not be applicable to pressure-sensitive adsorbent crystals, such as organic materials like MOFs, as they tend to deform due to the applied load.

Figure 7 - Schematic diagram illustrating the experimental set-up used for porosity measurement. The arrows indicate argon flow direction.
In addition to the characterization of porosity and crystal density of ZT, permeability of the adsorption bed is calculated using Darcian permeability given by

\[ \kappa = - \frac{Q \cdot \mu \cdot L}{A \cdot \Delta P}. \] (9)

Where \( \kappa \), \( Q \), and \( A \) are the Darcian permeability in m\(^2\), gas flow rate in m\(^3\)/sec, and cross sectional area to the gas flow in m\(^2\), respectively. Calculated permeability of the adsorption bed using Equation (9) is shown in Figure 9.
Figure 9 – Permeability of adsorption bed as function of density.

2.2 Determining Adsorption and Desorption Characteristics of Zeolite 13X

A dynamic vapor sorption (DVS) analyzer (DVS Vacuum, Surface Measurement Systems Ltd., London, UK), with weighing resolution of 0.1 \( \mu g \), was used to characterize the adsorption characteristics of \(~ 10 \text{ mg}~\) powdered ZT where the amount of pure water vapor was precisely controlled to change relative pressure (RP). Figure 10 shows adsorption/desorption isotherm measurement of ZT at 25 °C. Powdered ZT was dehydrated in high vacuum (< 1 Pa) at high temperature (> 300 °C) within the instrument prior to the measurement.
In addition to the adsorption isotherms, vapor transport characteristics of adsorbents is an important parameter as the performance of the adsorption based systems depends on the discharging kinetics. Intracrystalline diffusivity, $D_v$, of ZT can be calculated using the adsorption kinetics of ZT, shown in Figure 11, with the Fick’s 2nd law given by

$$\frac{\partial c}{\partial t} = D_v \cdot \frac{\partial^2 c}{\partial x^2}. \quad (10)$$

Assuming intracrystalline diffusivity, $D_v$, and vapor concentration, $c$, are constant, and zeolite crystals are spherical in geometry with radius $r$ of 1 μm, then Equation (10) in a spherical coordinate is
\[
\frac{\partial c}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left( D_v \cdot r^2 \cdot \frac{\partial c}{\partial r} \right) .
\]  

(11)

By assuming \( m \) (adsorbed phase mass) = 0 at \( t \) (time) = 0 and \( m = m_{\text{equil}} \) (equilibrium mass of adsorbed phase) at \( t = \infty \), and \( (\partial c/\partial r) = 0 \) at \( r = 0 \), Equation (11) becomes,

\[
\frac{m_t}{m_{\text{equil}}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left( \frac{1}{n^2} \right) \exp \left( -\frac{n^2 \cdot \pi^2 \cdot D_v \cdot t}{r^2} \right).
\]  

(12)

For short duration of time, Equation (12) further reduces to

\[
\frac{m_t}{m_{\text{equil}}} = \frac{6}{r} \sqrt{D_v \cdot \frac{t}{\pi}} < 0.2
\]

(13)

\[
0.2 < \frac{m_t}{m_{\text{equil}}} = \frac{6}{r} \sqrt{D_v \cdot \frac{t}{\pi}} - 3 \cdot D_v \cdot \frac{t}{r^2} < 0.8.
\]

For the calculation of the intracrystalline diffusivity, expression for \( 0.2 < m_t/m_{\text{equil}} < 0.8 \) was used, since the expression covers wider range of the adsorbed phase mass. Mass change at relative pressure of 2.4 %, marked in Figure 11, is used since this pressure range best matches with the ATB operating pressure. Due to fast surface adsorption of ZT at the beginning of vapor exposure, there is a rapid increase of mass in the first 10 minutes of each vapor pressure step as evident in Figure 11. This surface adsorption process ends in about 10 minutes followed by intracrystalline vapor diffusion within the ZT crystal. From this stated point as an initial point of the calculation (\( m = 0 \) and \( t = 0 \)), the intracrystalline diffusivity of ZT was calculated. Figure 12 shows \( m_t/m_{\text{equil}} \) as a function of \( \sqrt{t} \) determined from the 2.4 % relative pressure adsorption kinetics of ZT. The best fit second order polynomial equation from the experimental results shown in Figure 12 is

\[
\frac{m_t}{m_{\text{equil}}} = -1.1 \cdot 10^{-3} \cdot t + 7.27 \cdot 10^{-2} \sqrt{t} - 0.296
\]

(14)

27
Using the first order, $\sqrt{t}$, coefficient of Equation (14), the average intracrystalline diffusivity of ZT at the 2.4% relative pressure is calculated to be $4.61 \cdot 10^{-16}$ m$^2$/sec. This provides an order of magnitude estimation of the intracrystalline vapor diffusivity of ZT.

Figure 11 – Adsorption kinetics of ZT as function of water vapor pressure at 25 °C. Courtesy Xiansen Li of M.I.T.
Alternative to the adsorption isotherm measurements from DVS, a vapor sorption analyzer (TA Instrument, Q5000 SA) can also be used to characterize the adsorption capacity of ZT. Vapor sorption analyzer monitors the mass change of adsorbent with flowing nitrogen gas and vapor mixture with known humidity. However, hydrophilic adsorbents (e.g., ZT) cannot be regenerated within the instrument due to limited temperature supply of the sample chamber (80 °C). Powdered ZT sample was regenerated with 400 °C in air prior to transport to the sorption analyzer and characterized adsorption capacity of ZT using the instrument is shown in Figure 13.

Figure 12 – 2nd order polynomial fitting of $\frac{m_t}{m_{\text{equil}}}$ vs. $\sqrt{t}$ determined from Figure 11.
Figure 13 – Adsorption capacity of ZT measured with Sorption Vapor Analyzer.

A TGA (DISCOVERY TGA, TA instruments), with temperature accuracy of ± 1 °C and weighing accuracy of ± 0.1 %, was used to characterize desorption characteristics of ZT. Since the overall cycling efficiency (or charging efficiency) of the ATB system depends on the rate and the input power for desorption. Powdered ZT samples bearing 30 wt.% water were heated to different temperatures ranging from 150 °C to 350 °C in the TGA. In order to observe and measure desorption characteristics in-situ, the temperature was ramped at 40 °C/min, with nitrogen flowing gas. As evident in Figure 14, the threshold temperature required to dry powdered ZT completely was found to be between 250 – 300 °C, and the time required for
complete desorption was close to 10 minutes at 350 °C. Reduction in weight was determined to be ~23% beyond the threshold temperature, which corresponds to 30 wt.% initial uptake.

Note there is a discrepancy between the adsorption isotherm measured with DVS (Figure 10) and adsorption and desorption curves shown in Figure 13 and Figure 14, respectively. It is because powdered ZT was regenerated with vacuum and high temperature (> 300 °C) for the DVS measurements while vacuum was not used for the vapor sorption and TGA analyses. Although DVS measures complete adsorption isotherms, regeneration with vacuum may not be practical for the most of adsorption systems. It is to be noted that thermally unstable adsorbents require a more detailed characterization since they degrade at higher temperatures.

Figure 14 - Desorption characteristics of powdered ZT at 0 % RH.
2.3 Experimental Characterization of Enthalpy of Adsorption/Desorption of Zeolite 13X – Water Pair

Enthalpy of adsorption is an important parameter for the adsorption based heat storage systems since the amount of energy that can be stored within a system is a function of both adsorption isotherm and enthalpy of adsorption. The enthalpy of adsorption is measured most commonly in either of two ways: isosteric enthalpy of adsorption method and calorimetric measurement [35]. The isosteric enthalpy of adsorption is a thermodynamic relation derived from adsorption equilibriums measured in different temperatures with constant uptake, given by

\[ \Delta H_{\text{ads}} = R \left( \frac{d(\ln P)}{d \left( \frac{1}{T} \right)} \right)_m \]  

(15)

Where \( \Delta H_{\text{ads}} \), \( R \), \( P \), \( T \), and \( m \) represent the isosteric enthalpy of adsorption, gas constant, pressure, temperature, and uptake, respectively. Fitting the adsorption isotherms measured in a range of temperature with constant uptake in Equation (15), the isosteric heat of adsorption at the uptake can be estimated. However, calculating isosteric enthalpy of adsorption for hydrophilic adsorbents like ZT have serious inaccuracies at low relative pressures as adsorption isotherms overlap as evident in Figure 15. Thus, the enthalpy of adsorption associated with the initial adsorbed layer is most likely not possible to determine from Equation (15). For the calorimetric measurements, heat flow is directly measured during the adsorption process by introducing steps of small amount of vapor phase adsorbate within a calorimetric cell. Then, the enthalpy of adsorption is calculated using the first law of thermodynamics [35],

\[ dU = dQ_{\text{rev}} - dW_{\text{rev}} + u_{\text{ads}} dn \]  

(16)

Where \( dU \), \( dQ_{\text{rev}} \), \( dW_{\text{rev}} \), \( u_{\text{ads}} \), and \( dn \) are the change of the internal energy, reversible heat transfer with the surroundings, reversible compression work experienced by gaseous phase
against the external pressure, specific internal energy of vapor phase adsorbate, and amount of vapor phase adsorbate introduced during a step, respectively. However, due to the assumption of the ideal gas behavior and reversible heat and work transfers, this technique takes significant amount of time and becomes inaccurate at high pressures. Although the enthalpy of adsorption has been studied extensively [35-37], interactions between adsorbate and adsorbent are not fully understood. In this section, the enthalpy of desorption/adsorption of ZT – water pair is characterized to provide better understanding of interactions between the adsorbent and adsorbate as a function of the adsorbate loading, using the state of the art thermal analysis tool, Simultaneous Thermal Analyzer (STA).
2.3.1 Working Principles of Simultaneous Thermal Analyzer

For this study, a simultaneous thermal analyzer (STA 449 C, Netzsch) was used to characterize the enthalpy of desorption of ZT – water pair. STA is a thermal analysis tool capable of providing simultaneous enthalpy and mass scan of a sample. STA scans enthalpy change of a sample using differential scanning calorimetric (DSC) technique where heat flux is measured to raise the sample and well characterized reference temperature to a particular temperature with known ramping rate inside a controlled furnace. During the temperature change, the mass of the
sample is monitored precisely with thermogravimetric analyzer (TGA). A calibration curve associated with STA 449C enthalpy measurements is shown in Figure 16. DSC signals, in μV, obtained from the instrument is converted to heat flux, in mW, using the calibration shown below. Any undesired specific heat and thermal buoyancy effects from the sample crucible and the environment can be corrected with several baseline runs prior to the designated experiment.

Figure 16 – Sensitivity (Enthalpy) calibration plot of STA 449 C with Sapphire standard as function of temperature.
2.3.2 Experimental Characterization of Enthalpy of Desorption

To characterize the enthalpy of desorption, powdered ZT bearing ~ 30 wt.% initial uptake with dehydrated mass of 16.68 mg inside an aluminum sample crucible was ramped to 300 °C with 10 °C/min ramp rate from room temperature with purging nitrogen gas. Detailed experimental procedure is shown below:

a) Ramp to 350 °C with ramp rate of 10 °C/min
b) Isothermal at 350 °C for 1 hour
c) Ramp down to 30 °C with ramp rate of 10 °C/min
d) Isothermal at 30 °C for 1 hour
e) Ramp to 350 °C with ramp rate of 10 °C/min
f) Isothermal at 350 °C for 1 hour
g) Ramp down to 30 °C with ramp rate of 10 °C/min

The second ramp shown in the procedure e) is for the calculation of enthalpy change of the dehydrated ZT from the specific heat effect. And the purpose of isothermal conditions after each ramp was to stabilize the temperature. Prior to the experiment described, several baseline runs were done to correct the specific heat and thermal buoyancy mass effects from the sample crucible and the environment. DSC/TGA signals obtained during procedure a) and c) are used to calculate the enthalpy of desorption using following equations:

\[
q_1 = m_{ads}(t) \cdot C_{p,ads} \cdot \frac{dT}{dt} + m_{desorb} \cdot h_{desorb}(\omega) + m_{ZT} \cdot C_{p,ZT} \cdot \frac{dT}{dt} - m_{vapor \, out} \cdot h_{vapor}
\]

(17)
\[ q_2 = m_{zt} \cdot C_{p,zt} \cdot \frac{dT}{dt}. \]  

(18)

In Equations (17) and (18), \( \dot{q}, \, C_{p,ads}, \, dT/dt, \, \dot{m}_{desorb}, \, h_{desorb}(\omega), \, m_{zt}, \, C_{p,zt}, \, \dot{m}_{vapor \, out}, \) and \( h_{vapor} \) are the heat flux, specific heat of adsorbed phase, rate of temperature change over time, mass flux of desorbed vapor, specific enthalpy required for desorption, mass of ZT, specific heat of ZT, and mass flux and specific enthalpy of vapor going out of the sample crucible upon desorption. The desorbed vapor is assumed to be purged right away upon desorption, thus not effecting the heat flux measurements from its own specific heat. Since both \( \dot{m}_{desorb} \) and \( \dot{m}_{vapor \, out} \) are equal, the difference in the specific enthalpy for desorption and vapor going out of the crucible is defined as the enthalpy of desorption,

\[ \Delta h_{desorb}(\omega) = h_{desorb}(\omega) - h_{vapor}. \]  

(19)

And Equation (17) becomes

\[ \dot{q}_1 = m_{ads}(t) \cdot C_{p,ads} \cdot \frac{dT}{dt} + \dot{m}_{desorb} \cdot \Delta h_{desorb}(\omega) \]

\[ + m_{zt} \cdot C_{p,zt} \cdot \frac{dT}{dt}. \]  

(20)

The enthalpy of desorption is a function of desorbed mass since the initial adsorbed layer has stronger interaction with the adsorbent crystal with higher adsorption energy [36, 37]. Equation (20) represents the heat flux from the first ramp, described in procedure a), and equation (18) represents the heat flux from the second ramp. Heat flux from the first ramp has three contributing factors: the specific heat of ZT, the specific heat of adsorbed phase, and the enthalpy of desorption. In the second ramp, the heat flux has only one contributing factor, the specific heat of ZT, since ZT was dehydrated after the first ramp. Figure 17 shows representative DSC/TGA signals obtained from the experiment described. The heat flux from the specific heat of ZT in Equation (20) is eliminated using Equation (18) as shown below:
\[
\dot{Q}_{ads} = \dot{m}_{desorb} \cdot \Delta h_{desorb}(o) + m_{ads}(t) \cdot C_{p,ads} \frac{dT}{dt}
\]  

(21)

In Equation (21), \( \dot{Q}_{ads} \) represents the heat flux from the adsorbed phase and the enthalpy of desorption. Given that

\[
m_{ads}(t) = m_{initial} - m_{loss}(t)
\]

(22)

\[
\dot{m}_{desorb} = \frac{\Delta m}{\Delta t}
\]

(23)

where \( m_{initial} \), \( m_{loss}(t) \), and \( \Delta m/\Delta t \) are the weight of the initial adsorbed phase (5.004 mg), desorbed mass at time \( t \), and desorption mass flux during a segment of \( time_2 - time_1 = \Delta t \), respectively. Due to the start-up effect associated with the initial heating region, signals obtained during the first 4 - 5 minutes of the initial heating were disregarded [38]. For the calculation of the enthalpy of desorption, the heat fluxes from the two ramps were divided into 10 °C segments (from 70 °C to 350 °C). It was assumed that the adsorbed phase water has the specific heat of bulk phase liquid water (Figure 18), the enthalpy of desorption was evaluated by applying the trapezoidal numerical integration over 10 °C segments as shown in Figure 19.

It is clear from Figure 19 that the required enthalpy of desorption increases as desorption continues. The highest enthalpy of desorption measured is 2.82 times of the enthalpy of vaporization of water (2256 kJ/kg at the atmospheric pressure) at \( m_{desorbed}/m_{initial} = 98 \% \).

The initial adsorbed layer within ZT crystal during the adsorption process has the higher adsorption energy due to the stronger affinity to water [36, 37]. The average enthalpy of desorption during the temperature ramping of 70 to 350 °C, for last ~27 wt.% desorbed phase, was 3077.2 kJ/kg and this is 1.36 ± 0.05 times the enthalpy of vaporization of water. Assumption of the physical state of the adsorbed phase was made prior to the calculation. In order to
understand the trend shown in Figure 19 in more detail, further investigation in the characterization of the physical state of adsorbed phase is indeed necessary.

Figure 17 – Representative DSC/TGA signals obtained from ZT desorption experiment.
Figure 18 – Specific heat of saturated liquid water as function of temperature [39].
2.3.3 Derivation of Enthalpy of Adsorption

In the previous section, the enthalpy of desorption of water – ZT pair was experimentally determined. In this section, derivation of the enthalpy of adsorption from the enthalpy of desorption is present using the first law of thermodynamics for a cycle given by

\[ \oint dE = \oint dQ + \oint dW, \]  

where \( E \), \( Q \), and \( W \) are the energy, heat and work transfers, respectively. Assume dehydrated ZT went through an adsorption, desorption, and cooling down cycle as shown in Figure 20. For
simplicity, the cycle was modeled as follows: the adsorption process is carried out in the constant temperature of 70 °C and the desorption process is done during the temperature ramping from 70 to 350 °C. After the desorption process, ZT is cooled down to the initial state. Drawing a control volume (CV) around the sample crucible as indicated in Figure 21, the change of the energy due to the constant temperature adsorption process (process a to b) of the CV can be expressed as,

\[ E_b - E_a = - \int m_{ads} \cdot h_{ads}(\omega) \, dt + \int m_{vapor \, in} \cdot h_{vapor} \, dt. \] (25)

Since the boundary of the CV is fixed and the pressure inside the CV is equal to the pressure outside of the CV, work transfer to the CV is always zero. \( m_{ads}, h_{ads}(\omega), m_{vapor \, in}, \) and \( h_{vapor} \) are the adsorbed mass flux, specific enthalpy for adsorption, and mass flux and enthalpy of incoming vapor, respectively. Since both the adsorbed and vapor mass fluxes are equal, the enthalpy of adsorption is defined as

\[ \Delta h_{ads}(\omega) = h_{ads}(\omega) - h_{vapor}. \] (26)

And Equation (26) becomes

\[ E_b - E_a = - \int m_{ads} \cdot \Delta h_{ads}(\omega) \, dt. \] (27)

For the desorption process (process b to c), assume desorbed vapor purged away upon desorption. As derived in the previous section, the change in the energy within the CV during the desorption process is

\[ E_c - E_b = \]

\[ - \int m_{des} \cdot \Delta h_{des}(\omega) \, dt + \int m_{ads}(t) \cdot C_p,ads \cdot \frac{dT_{des}}{dt} \, dt \]

\[ + \int m_{ZT} \cdot C_p,ZT \cdot \frac{dT_{des}}{dt} \, dt. \] (28)

42
Similarly for the cooling down process (process c to a), assume the environment is inert (e.g., no vapor present). The change in the energy of the CV is

\[ E_a - E_c = \int m_{zT} \cdot C_{p,zT} \cdot \frac{dT_{cooling}}{dt} \, dt. \]  

(29)

The change of the energy for the cycle should be zero,

\[ (E_b - E_a) + (E_c - E_b) + (E_a - E_c) = 0. \]  

(30)

Therefore,

\[ \int \dot{m}_{ads} \cdot \Delta h_{ads}(\omega) \, dt \]

\[ = \int \dot{m}_{des} \cdot \Delta h_{des}(\omega) + m_{ads}(t) \cdot C_{p,ads} \cdot \frac{dT_{des}}{dt} \, dt. \]

(31)

The right hand side of the Equation (31) is the energy associated with the adsorbed phase specific heat and the enthalpy of desorption during the desorption process, which was characterized experimentally from 70 to 350 °C. The average enthalpy of adsorption at 70 °C is then

\[ \Delta h_{ads,avg} = \frac{1}{m_{ads}} \int \dot{m}_{des} \cdot h_{des}(\omega) + m_{ads}(t) \cdot C_{p,ads} \cdot \frac{dT_{des}}{dt} \, dt. \]  

(32)

Where \( m_{ads} \) is the amount of adsorbed water that desorbed (4.50 mg) from temperature ramping of 70 to 350 °C during the desorption experiment. The average enthalpy of adsorption carried out in the constant temperature of 70 °C calculated using Equation (32) is 3804.9 kJ/kg (represents average over initial ~ 27 wt.% uptake of ZT) which corresponds to 1.69 times of the enthalpy of vaporization of water (2256 kJ/kg) and 1.24 times of the enthalpy of desorption (3077.2 kJ/kg). This is as expected since the desorption process was carried out in higher temperature range (70 to 350 °C). Chapter 2.3 describes novel experiment technique for characterizing the enthalpies of adsorption and desorption. If the specific heat of adsorbed phase is well characterized, the
enthalpies associate with the adsorption and desorption processes as function of adsorbate loading can be calculated accurately using the technique.

Figure 20 – Representative adsorption/desorption cycle. $Q_{\text{adsorption}}$ and $Q_{\text{desorption}}$ are heat fluxes due to adsorption and desorption processes, respectively. $Q_{\text{Cp,ZT}}$ and $Q_{\text{Cp,ads}}$ are heat fluxes associated with specific heat effect of zeolite and adsorbed phase, respectively.
Figure 21 – Description of cycle present in Figure 20.
2.4 Experimental Characterization of Enhanced Thermal Transport Properties of Adsorptive Materials with Carbon Nano-Materials

Typical adsorbents exhibit poor thermal conductivity (0.1 - 0.3 W/mK for ZT, see Figure 25), matching those of typical ceramics and insulators. This is an undesirable characteristic for typical adsorption systems including thermal and gas storage, and separation systems.

This section presents a systematic study of carbon nano-materials, functionalized multi-walled carbon nanotube (fCNT) and few layer graphene (GR), as thermal binders to increase the effective thermal conductivity of ZT composite. A detailed experimental characterization and theoretical framework of thermal transport behavior in ZT composite will also be discussed.

2.4.1 Sample Preparation

fCNT and GR binders were synthesized, as reported [40]. The thermophysical properties of synthesized binders are presented in Table 1. Then, ZT-fCNT and ZT-GR composites were fabricated, first by mixing them in an ethanol solution, followed by tip sonication. Then, the mixture was pressed in the form of circular pellets (dia. = 12.7 mm) using a hydraulic press. The crystallinity of ZT was remained intact after densification process, as evident in XRD analysis shown in Figure 22.

Adsorption capacity is one of the most important parameters for the adsorption-based systems. Previous work on enhancing the effective thermal conductivity of the adsorbent-binder composites show significant reduction in the overall adsorption capacity [41]. Therefore, in this study, weight contribution of thermo-binder was limited to 3 wt.%, as evident in Figure 23 and Figure 24. The TGA was used to analyze the weight contribution of GR, where ZT-GR composite was first dried at 350 °C in an inert gas. The flowing gas was then switched to air to
burn the carbonaceous materials, such as fCNT or GR. The net mass of carbon nano-material in the composite material was found to be close to 3 wt.%. A vapor sorption analyzer (TA Instrument, Q5000 SA) was used to characterize the adsorption capacity of each sample. A negligible decrease in the adsorption capacity of ZT-fCNT and ZT-GR composites were observed, with net adsorption capacities comparable to a pure ZT composite, as shown in Figure 24. In addition to the adsorption capacity measurements, a BET analyzer (Quantachrome, Autosorb IQ2 Surface Sorption Analyzer) was used to measure the surface area and micro-pore volume of each sample using nitrogen, as tabulated in Table 2, where no reduction in both surface area and micro-pore volume was observed.
Thermal additives

<table>
<thead>
<tr>
<th></th>
<th>fCNT</th>
<th>GR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>~ 3000 W/mK</td>
<td>~ 3000 W/mK</td>
</tr>
<tr>
<td>Size</td>
<td>5 nm dt. &amp; 2 μm length</td>
<td>2 μm dt.</td>
</tr>
<tr>
<td>Dimensionality</td>
<td>1D</td>
<td>2D</td>
</tr>
<tr>
<td>Thermal resistance</td>
<td>~ 8x10^-8 m^2K/W</td>
<td>~ 8x10^-8 m^2K/W</td>
</tr>
</tbody>
</table>

Table 1 - Thermophysical properties of fCNT and GR [42-44].

Figure 22 - XRD patterns of ZT before (black) and after (red) densification using hydraulic press. Courtesy Sungwoo Yang of M.I.T.
Figure 23 – TGA plot of ZT-GR composite. Sample was initially ramped to 350 °C and temperature was held for 2 hours in nitrogen gas environment to dehydrate ZT. Then flowing gas was switched to air and temperature was ramped to 800 °C to burn carbon nano-materials.
Figure 24 - Adsorption capacity of ZT, ZT-fCNT, and ZT-GR at 10% RH. A small reduction (2-3 %) in adsorption capacity of ZT-fCNT and ZT-GR composites are due to weight contribution of fCNT and GR binders.
<table>
<thead>
<tr>
<th></th>
<th>N₂ Surface area</th>
<th>Micro-pore Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m²/g)</td>
<td>(cm³/g)</td>
</tr>
<tr>
<td>Zeolite 13X (ZT)</td>
<td>661</td>
<td>0.280</td>
</tr>
<tr>
<td>ZT/3 wt.% fCNT</td>
<td>667</td>
<td>0.281</td>
</tr>
<tr>
<td>ZT/3 wt.% GR</td>
<td>659</td>
<td>3...:</td>
</tr>
</tbody>
</table>

Table 2 - Nitrogen surface area and micro-pore volume of ZT, ZT-fCNT, and ZT-GR. Surface area and micro-pore volume measurements confirm fCNT and GR do not block micro-pore of adsorbent ZT.

2.4.2 Measurement of Thermal Conductivity

Thermal conductivity is a function of thermal diffusivity, specific heat, and density, which can be expressed as,

\[ k_{\text{eff}} = \alpha \cdot c_p \cdot \rho, \]  

(33)

where \( k_{\text{eff}} \), \( \alpha \), \( c_p \), and \( \rho \) are effective thermal conductivity, thermal diffusivity, specific heat, and density of a composite material, respectively. The thermal diffusivity of ZT, ZT/fCNT, and ZT/GR composites was measured using Laser Flash Analyzer (Netzsch LFA 457 MicroFlash system) provides \( \pm 3\% \) accuracy. The laser flash measures the temperature rise on the backside of the sample after a laser pulse irradiates the front side. The thermal diffusivity is characterized based on the kinetics of thermal transport. Consequently, if the thermal diffusivity is higher, the rise in temperature is faster. Thermal diffusivity can be calculated by
\[
\alpha = 0.1388 \cdot \frac{d^2}{t_{1/2}},
\]

where \( d \) is the thickness of the sample and \( t_{1/2} \) is the half-time to attain the maximum temperature due to the laser-pulse heating [45].

Each sample was dried inside the Laser Flash Analyzer with 300 °C in inert gas (Ar) prior to the measurements to eliminate the effect of adsorbed water in ZT. The specific heat of each composite was then measured using Differential Scanning Calorimeter (DSC, Mettler Toledo). The specific heat of each sample was measured to be around 0.9 J g\(^{-1}\) K\(^{-1}\), which is well matched with a previous study [46]. A density measurement of each sample was made after drying it in 450 °C for 6 hours. The experimentally determined average thermal conductivity of dry ZT, ZT-fCNT, and ZT-GR composites are shown in Figure 25. Interestingly, the enhancement in the effective thermal conductivity was only observed with GR, which is about 30 % enhancement.
2.4.3 Thermal Transport Modeling

To understand the enhancement in the thermal transport characteristics of ZT/binder composites, a theoretical analysis was carried out using a modified effective medium theory developed by Nan et al. [47]. This approach assumes no percolation of the thermal binders in ZT matrix and a constant interfacial resistance between the ZT matrix and thermal binders. As introduced by Nan et al., the effective thermal conductivity of the composite with equally sized ellipsoidal particles can be written as

Figure 25 – Experimentally measured effective thermal conductivity of ZT, fCNT-ZT, and GR-ZT composites.
$\begin{align*}
K_{11}^* &= K_{22}^* = \\
&= k_m \cdot \frac{2 + f[\beta_{11}(1-L_{11})(1+<\cos^2 \theta>) + \beta_{33}(1-L_{33})(1-<\cos^2 \theta>)]}{2 - f[\beta_{11}L_{11}(1+<\cos^2 \theta>) + \beta_{33}L_{33}(1-<\cos^2 \theta>)]},
\end{align*}$

(35)

$\begin{align*}
K_{33}^* &= k_m \cdot \frac{1 + f[\beta_{11}(1-L_{11})(1-<\cos^2 \theta>) + \beta_{33}(1-L_{33})<\cos^2 \theta>]}{1 - f[\beta_{11}L_{11}(1-<\cos^2 \theta>) + \beta_{33}L_{33}<\cos^2 \theta>]},
\end{align*}$

(36)

where

$$\beta_{ii} = \frac{K_{ii}' - K_m}{K_m + \lambda_{ii}' (K_{ii}' - K_m)},$$

(37)

$$<\cos^2 \theta> = \frac{\int \rho(\theta) <\cos^2 \theta> \sin \theta d\theta}{\int \rho(\theta) \sin \theta d\theta},$$

(38)

and $L_{ii}$ is the geometrical shape factor [48] given as

$$\begin{align*}
L_{11} &= L_{22} = \begin{cases} 
\frac{p^2}{2(p^2-1)} - \frac{p}{2(p^2-1)^{3/2}} \cosh^{-1} p, & \text{for } p > 1, \\
\frac{p^2}{2(p^2-1)} - \frac{p}{2(1-p)^{3/2}} \cos^{-1} p, & \text{for } p < 1,
\end{cases}
\end{align*}$$

(39)

$$L_{33} = 1 - 2 \cdot L_{11}.$$

In Equations (35) and (36), $k_m$ is the thermal conductivity of the matrix phase (e.g., ZT) and $f$ is the volume fraction of additives (i.e., thermal binders). Transverse direction components are represented with subscripts 11 and 22, and 33 represents components with longitudinal direction. $\rho(\theta)$ is a distribution function describing orientation of ellipsoidal particles within a matrix and $<\cos^2 \theta>$ is equal to 1/3 for a random distribution of ellipsoidal particles. Schematics illustrating the thermal resistance network and equivalent thermal conductivities in both transverse and longitudinal directions for fCNT and GR are presented in Figure 26 and Figure 27,
respectively. For fCNT, the thermal resistance network across the transverse direction (11 or 22 direction) can be written as

\[ 2 \cdot R_k + \frac{d_{f\text{cnt}}}{k_{f\text{cnt}}} = \frac{d_{f\text{cnt}}}{k_{11}^c}, \]  

(40)

then, \( K_{11}^c \) can be simplified as

\[ K_{11}^c = \frac{k_{f\text{cnt}}}{1 + \frac{2 R_k k_{f\text{cnt}}}{d_{f\text{cnt}}}}, \]  

(41)

Similarly, the thermal resistance network for longitudinal direction (33 direction) can be represented as

\[ 2 \cdot R_k + \frac{L_{f\text{cnt}}}{k_{f\text{cnt}}} = \frac{L_{f\text{cnt}}}{k_{33}^c}, \]  

(42)

where

\[ K_{33}^c = \frac{k_{f\text{cnt}}}{1 + \frac{2 R_k k_{f\text{cnt}}}{L_{f\text{cnt}}}}, \]  

(43)

Since fCNT has a high aspect ratio, typically around 1000, the geometrical shape factors can be reduced to

\[ p > 1000 \]  

(44)

\[ L_{11} = L_{22} = \frac{1}{2} \]

\[ L_{33} = 0. \]

Assuming a random dispersion of fCNT with an aspect ratio around 1000 within a ZT matrix, Equations (35) and (36) reduce to

\[ \frac{K_{ef\text{cnt}}}{K_m} = \frac{3 + f^* (\beta_{11} + \beta_{33})}{3 - f^* \beta_{11}}, \]  

(45)

with \( \beta_{11} = \frac{2 (K_{11}^c - K_m)}{K_{11}^c + K_m} \) and \( \beta_{33} = \frac{K_{33}^c}{K_m} - 1, \)

where \( K_{ef\text{cnt}} \) is the effective thermal conductivity of the ZT/fCNT composite.
For GR, the thermal resistance network across the transverse direction can be written as

\[ 2 \cdot R_k + \frac{L_{GR}}{k_{GR}} = \frac{L_{GR}}{K_{11}^c} \]  

(46)

then, \( K_{11}^c \) can be simplified as

\[ K_{11}^c = \frac{k_{GR}}{1 + \frac{2R_k k_{GR}}{L_{GR}}} \]  

(47)

Similarly for the longitudinal direction,

\[ 2 \cdot R_k + \frac{L_{GR}}{k_{GR}} = \frac{L_{GR}}{K_{33}^c} \]  

(48)

and then

\[ K_{33}^c = \frac{k_{GR}}{1 + \frac{2R_k k_{GR}}{L_{GR}}} \]  

(49)

The aspect ratio of GR is very small, typically around 0.001, and the geometrical shape factors reduce to

\[ p < 0.001 \]

\[ L_{11} = L_{22} = 0 \]

\[ L_{33} = 1. \]

Assuming a random dispersion of GR with an aspect ratio around 0.001 within a ZT matrix, Equations (35) and (36) reduce to

\[ \frac{K_{eGR}}{K_m} = \frac{3 + 2f \beta_{11}}{3 - f \beta_{33}} \]  

(51)

with \( \beta_{11} = \frac{K_{11}^c}{K_m} - 1 \) and \( \beta_{33} = 1 - \frac{K_m}{K_{33}} \),

where \( K_{eGR} \) is the effective thermal conductivity of the ZT/GR composite.
Figure 26 – Schematic illustration of composite unit cell of fCNT coated with thin interfacial thermal barrier. The transverse and longitudinal equivalent thermal conductivities, $K_{11}^c$ and $K_{33}^c$, of this composite unit cell can be directly obtained with resistance network model. $d_{fCNT}$, $L_{fCNT}$, $R_k$, $k_{fCNT}$ are diameter, length, interfacial thermal resistance, and intrinsic thermal conductivity of fCNT, respectively.
Figure 27 – Schematic illustration of composite unit cell of GR coated with thin interfacial thermal barrier. The transverse and longitudinal equivalent thermal conductivities, $K_{33}^c$ and $K_{53}^c$, of this composite unit cell can be directly obtained with resistance network model. $t_{GR}$, $L_{GR}$, $R_k$, $k_{GR}$ are thickness length, interfacial thermal resistance, and intrinsic thermal conductivity of GR, respectively.

Thermophysical properties of both fCNT and GR are tabulated in Table 1. For simplicity, the interfacial thermal resistance between thermal binders and ZT matrix was assumed to be a constant, $8 \times 10^{-8}$ m$^2$K/W [43].

In addition to the mathematical derivation of thermal transport modeling, contact area of each thermal binder (fCNT and GR) with ZT matrix was analyzed visually using a SEM (JEOL 6010LA SEM), as shown in Figure 28. The model developed by Nan et al. [47] assumes perfect contact of binders with matrix phase. However, since the ZT composite is a packed sample of porous particles, a modification to the Nan model is required. The contact area ratio of each binder within the ZT matrix was extracted from various SEM images, see Figure 29. As evident
from the SEM images, the contact area for the GR was found to be significantly higher than that of the fCNT binder. As a result, modifications to the thermal transport model have been made as shown in Figure 30, where the volume fraction was corrected with the contact area ratio. It was observed from visual analysis that the fCNT binders tends to either make contact with the ZT matrix or not making contact at all. However, for the GR binders, most of the GR makes contact with the ZT matrix, but only small portion of the binders were not making the contact. Therefore, in addition to the correction of the volume fraction, geometry of the GR binder was modified based on the contact area ratio. Modified model from Equations (45) and (51) is plotted in Figure 31, which shows a good agreement with experimental results. The modified model was used to predict 3, 5, 10, and 15 wt.% binder content in the composite material as shown in Figure 32, where GR binder show significant improvement in the effective thermal conductivity of the composite material. The maximum possible thermal conductivity achievable with the 15 wt.% GR binder and the 15 wt.% fCNT binder are 0.786 and 0.5845 W/mK, respectively.
Figure 28 – Representative SEM images (red area: not contacting, blue area: contacting with ZT matrix)

Figure 29 – Contact area ratio for ZT-fCNT and ZT-GR composites (for more detail, see Appendix A – Determination of Contact Area Ratio of fCNT and GR Binders in ZT Matrix).
Figure 30 - Schematics of contact area ratio for both fCNT and GR.

\[ f_{\text{fCNT}} = \text{Contact Ratio} \cdot f_{\text{volume}} \]

\[ f_{\text{GR}} = \text{Contact Ratio} \cdot f_{\text{volume}} ; L_{\text{GR}} = \text{Contact Ratio} \cdot L \]
Figure 31 - Thermal conductivity vs. Density (experimental data with theoretical prediction).
Figure 32 - Theoretical predictions for effective thermal conductivity of ZT-fCNT and ZT-GR composites.
2.5 Summary

In this chapter, systematic characterizations of the adsorptive material, ZT, was carried out. This includes determination of the average porosity, crystal density, and permeability of the hydraulically-compressed adsorbent samples, characterizing the kinetics during the adsorption/desorption processes and characterization of the enthalpies of adsorption/desorption. Experimentally determined the average enthalpy of desorption for ZT – water pair was 3077.2 kJ/kg which is about 1.36 times the enthalpy of vaporization of water at the atmospheric pressure. And the average enthalpy of adsorption for ZT – water pair at 70 °C, representing initial ~ 27 wt.% uptake, was derived from the energy balance, 3804.9 kJ/kg. If one characterizes the thermophysical properties of the adsorbed phase, the enthalpies associated with the adsorption and desorption processes can be well characterized using the novel experiment technique described.

Enhancement in the effective thermal conductivity of adsorbent-binder composite using the carbon nano-materials was also studied extensively. As evident from the surface area and adsorption analyses, carbon-nano-materials did not contribute into the reduction of adsorption capacity while increasing the effective thermal conductivity of 6 to 25 % with the GR binder. A theoretical model was developed based on the effective medium approach developed by Nan et al. [47], which showed good agreement with the experimental results. Also theoretical predictions were made with the model, where GR was predicted to enhance the effective thermal conductivity of the ZT-GR composite material, by ~ 200 % with the addition of 15 wt.%. While a detailed characterization of adsorption and thermal transport was presented in this chapter, the fabrication of adsorption stacks made using ZT and the experimental characterization of vapor transport will be discussed in in the following chapter.
3. Experimental Characterization of Adsorption Stacks

The chapter describes the fabrication and characterization of the adsorption stacks to demonstrate enhanced heat and mass transport. As a practical and scalable alternative to the advanced carbon nano-material binders, we selected commercially available, highly porous (> 95%), copper foam structures as a structural binder for the fabrication of the adsorption bed. Lab-scale adsorption analyzers, such as BET sorption analyzers and thermogravimetric vapor analyzers, are limited by the maximum mass (< 20 mg) of the sample which can be characterized, which is significantly smaller than the mass of a single stack, ~20 g. Due to this limitation of lab-scale sorption analyzers, an experimental characterization methodology was developed to evaluate vapor uptake performance of a single-layer adsorption stack.

3.1 Thermal and Vapor Transport Characterization of Single-Layer Adsorption Stack with High-k Copper Foam

Although GR binder contributes close to 25% enhancement in the overall thermal conductivity of ZT composite without reduction in the adsorption capacity, the scalability of carbon-based nano-materials is an immediate concern for the demonstration of the ATB performance. In addition to scalability, a significant enhancement in thermal conductivity was observed only at high composite densities (> 1000 kg/m³). Therefore, copper foams (Copper foam, Shanghai Winfay New Material Co., Ltd) with porosities in excess of 95%, an average density close to 306 kg/m³, a characteristic pore size of 270 μm, and an average thermal conductivity greater than 3 W/mK, was selected for the performance characterization of an adsorption stack. The
following sections describe the fabrication methodology, thermal and adsorption characterization of the ZT-embedded copper foam structures.

3.1.1 Sample Fabrication

A ZT-copper foam composite layer (Figure 33) was prepared using the following procedure. First, a ZT suspension was prepared with DI water, then the copper foam was immersed into the suspension. Excessive solvent was evaporated by heating the solution on a hot plate. The dehydrated density of ZT within the copper foam was determined to be ranging between 500 to 670 kg/m$^3$. The thermal conductivity of the fabricated composite structure was measured to be around 3.7 W/mK using a steady-state conduction method [49], which is almost 100 times higher than that the pure ZT composite of similar density. A single-layer adsorption stack (dehydrated ZT mass of 1.71 g) with copper foam binder was fabricated following the described method in square dimension with area of $1.78 \times 10^{-3} \pm 3.1 \times 10^{-5}$ m$^2$, thickness of $1.96 \pm 0.04$ mm, and dehydrated ZT density of $529 \pm 16$ kg/m$^3$, as shown in Figure 34. The fabricated single-layer adsorption stack was attached with a thermal epoxy (Duralco 133, Cotronics Corp.) on to a high thermal-mass heat-sink copper block, which was interfaced with a coolant loop and a cartridge heater. The purpose of the heat sink was to minimize thermal transport limitations during experiments. This arrangement allows vapor to be adsorbed only from the top exposed surface of the single-layer since the back side was attached to the heat sink using the thermal epoxy.
Figure 33 – Fabrication of ZT+Cu foam composite. a) Cu foam. b) ZT-DI suspension. c) Fabricated sample following fabrication methodology discussed in 3.2.1. Courtesy Jianjian Wang and Xiaobo Li of M.I.T.
3.1.2 Performance Characterization

The fabricated single-layer stack was tested inside a vacuum environmental chamber; a schematic is shown in Figure 35. The prepared single-layer stack was interfaced with a coolant loop, thermocouples, and a cartridge heater inside the chamber. The experimental procedure is as follows:

a) Heat sample to ~90 °C in high vacuum (< 1 Pa) for >1 hour for desorption

b) Cool sample to <30 °C in high vacuum (< 1 Pa) using the coolant loop maintained at a low temperature (25 °C)

c) Introduce saturated vapor (T_\text{sat} = \text{Room Temperature}) while maintaining the heat sink at 25 °C with coolant line

d) Maintain a pressure of 1500 Pa using pressure-regulating valve until adsorption stack saturates completely
The pressure profile inside the vacuum chamber during the adsorption experiment, which was used to determine discharge performance of the single stack, is plotted in Figure 36. The pressure trend in time captured the sample saturating only in ~10 minutes during the experiment. The transient response of the single layer was monitored using an Infrared (IR) camera during the experiment, as shown in Figure 37. IR visualization used in the experiment was fully calibrated in the range of temperature interested, 20 °C to 97 °C, thus providing quantitative measurements. See Appendix B – Calibration of IR Measurements for more detail. The first 5 minutes of the adsorption experiment is presented in Figure 37, which represents rapid heat dissipation of the single-layer stack with high thermal conductivity binder to the copper heat sink which was kept at temperature of 25.5 ± 0.4 °C.
Figure 35 – Schematic diagram of vacuum environmental chamber system.
Figure 36 – Adsorption rate vs. Time shown for the adsorption experiment. The accuracy of pressure measurement is 0.5%.
Figure 37 - Transient response of fabricated single layer monitored using IR camera, first 5 minutes of adsorption experiment. (IR analysis was validated experimentally, see Appendix B – Calibration of IR Measurements).
To calculate adsorption rates, vapor pressure was periodically supplied as shown in Figure 36. The adsorption rates were evaluated from changing vapor pressure due to spontaneous adsorption of the sample in the chamber using the van der Waals equation of state,

\[
\left( p + \frac{n^2 \cdot a}{V^2} \right) \cdot (V - n \cdot b) = n \cdot R \cdot T
\]  

(52)

where \( a \) and \( b \) are 0.547 Pa \( \cdot \) m\(^3\) and 30.52e-6 m\(^3\)/mol, respectively. \( p \) is the chamber pressure in Pascal, \( n \) is the mole number of water vapor in mol, \( V \) is the volume of the chamber, 0.067 \( \pm \) 0.001 m\(^3\), \( R \) is the universal gas constant, 8.314 J-K/mol, \( T \) is the average gas temperature inside the chamber in Kelvin, 296.7 K. The compressibility factor, \( Z \), of water vapor in the pressure range of 1 to 1700 Pa and the temperature range of 290 to 350 K is between 1 and 0.999 [39]. Therefore, the van der Waals gas assumption should be accurate. The uptake rate is then can be calculated using following expression:

\[
\text{adsorption rate} = \frac{\Delta m}{\Delta t}.
\]  

(53)

Where reduction of vapor phase mass within the chamber, \( \Delta m \), between two points (from \( P_1 \) to \( P_2 \)) due to simultaneous adsorption can be evaluated using Equation (52) by knowing the molar mass of the water, 18.015 g/mol. And \( \Delta t \) is the duration of time for the pressure decrease from \( P_1 \) to \( P_2 \). The calculated adsorption rates, shown in Figure 36, reduce drastically over time. The total adsorbed water during the adsorption experiment from 1.34 to 8 minutes was 257 \( \pm \) 20.5 mg which corresponds to adsorption capacity of 15 \( \pm \) 1.15 wt.\%, and heating and cooling capacities of 880 \( \pm \) 70.2 J and 635 \( \pm \) 50.6 J (calculated based on the average enthalpy of adsorption from 2.3.3 and the enthalpy of vaporization of water at 1500 Pa), respectively. Remaining uncharacterized adsorption capacity of \( \sim \) 20 wt.% is most likely saturated before reaching the
isobaric condition of 1500 Pa (before 1.34 minutes). If one can introduce step change in the vapor pressure within the chamber followed by periodic vapor supply, the full range of the adsorption rate can be characterized. The adsorption rates, shown in Figure 36, reduce drastically over time. In practice, it is indeed necessary to throttle the vapor pressure during operation to spread out the adsorption rate evenly.

3.2 Summary

Performance characterization of the single-layer adsorption stack fabricated with highly conductive porous copper foam was carried out. Due to the limitation of the lab scale sorption analyzers, the novel experimental procedure characterized a macro-sized adsorption stack’s vapor uptake performance. Temperature profile, discharging performance, adsorption rate, and heating and cooling capacities of the single-layer adsorption stack were demonstrated and found that 10 minutes was sufficient time to saturate a 2 mm thick adsorption stack with density of 529 kg/m³ at vapor pressure of 1500 Pa.
4. Conclusion and Future Work

4.1 Conclusion

In this thesis, we experimentally investigated the adsorption properties and the thermal and vapor transport characteristics of zeolite 13X for the development of the advanced thermo-adsorptive battery (ATB). We are developing a compact and light-weight advanced thermal storage system using advanced adsorptive materials in combination with carbon nano-materials for efficient heat dissipation. While adsorption-based energy storage systems have received significant attention due to recent advances in adsorptive materials such as modified zeolites and MOFs, the poor transport characteristics of these advanced materials limits their application in energy storage. A detailed characterization and enhancement of the overall transport processes are necessary, and they are addressed in this thesis.

Detailed material characterizations of the adsorptive material, zeolite 13X, include measurements of porosity, crystal density, Darcian permeability, enthalpies associated with adsorption and desorption processes, micro-pore and surface area measurements, surface chemistry, and thermal transport properties of ZT composites were discussed in this thesis. The average enthalpy of desorption was experimentally determined, 3077.2 ± 112 kJ/kg, using the novel experiment technique. And the average enthalpy of adsorption was calculated, 3804.9 kJ/kg, from the enthalpy of desorption with energy balance. A theoretical model was developed, based on the effective medium approach [47], to predict the effective thermal conductivity of the ZT composite with carbon nano-material binders, fCNT and GR. Both from the theory and experiments, the GR binder outperformed the fCNT binder. Based on the developed thermal transport model, further predictions have been made as shown in Figure 32, where the GR binder
increases the effective thermal conductivity of the ZT composite by ~ 200 % with the addition of 15 wt. %.

Experimental characterization and development of an adsorption stack with enhanced heat transport characteristics were discussed in detail. Using the novel experimental procedure, temperature profile, discharging performance, adsorption rate, and heating and cooling capacity of the stack were presented. Consequently, this thesis can serve as a framework for the development and characterization of adsorption-based thermal storage systems.

4.2 Future Work

Besides the characterization of the thermophysical and transport properties of adsorptive materials for the development of the adsorption systems, characterizing the physical properties of the adsorbed phase is crucial. The state of the adsorbed phase is unknown: often researchers assume the state to be a liquid phase [50-52], while others consider it to be a gaseous phase [53, 54]. It could also be an intermediate state [55]. Although the physical state of the adsorbed phase may vary from adsorbent to adsorbent or by types of adsorption isotherms, understanding the state of the adsorbed phase would provide better understanding to the materials engineers who design and develop adsorptive materials. In addition to that, directly measuring the enthalpy of adsorption using a STA interfaced with vapor source and study interactions between adsorbate and adsorbent for different types of adsorptive materials will help us understand the adsorption/desorption processes.
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Appendices

Appendix A – Determination of Contact Area Ratio of fCNT and GR Binders in ZT Matrix

Various SEM images were analyzed by Sungwoo Yang of M.I.T. to determine the contact area ratio for both fCNT and GR binders in the range of composite density, see Figure 29 – Contact area ratio for ZT-fCNT and ZT-GR composites (for more detail, see Appendix A – Determination of Contact Area Ratio of fCNT and GR Binders in ZT Matrix). Figure 29. In Figure A 1 and Figure A 2, the blue area corresponds to the area that is in contact with the ZT matrix, and the red area is the area of the binder that is not in contact with the ZT matrix. The visualization of the contact (blue area) and non-contact (red area) areas was done with Photoshop, and the area ratios were extracted using a code written in Matlab.

![Figure A 1 - Example of contact ratio analysis based on SEM image of fCNT-ZT composite.](image-url)
Figure A 2 – Example of contact ratio analysis based on SEM image of GR-ZT composite.
Appendix B – Calibration of IR Measurements

Infrared (IR) measurements are often used for qualitative analysis, but if calibrated well, they could be used as a quantitative measurement tool. The zeolite 13X – Cu foam composite sample used for the single layer testing shown in Chapter 3.1 was used to validate IR measurements. 2 thermocouples (Omega) with accuracy of ± 0.2 °C were attached on the surface of ZT – Cu foam composite as shown in Figure A 3. Environment of the sample during the calibration was set to 1300 – 1500 Pa vapor pressure which generates very close condition for an adsorption experiment. The surface temperature of the sample was imaged through a Sapphire viewport with an IR camera (SC 6000, FLIR Systems). Signals (counts) obtained from the camera was then plotted as a function of the measured surface temperature of the sample, see Figure A 4. Plotted relation between the signals and the actual surface temperature was used to measure the temperature profile of the sample during the adsorption experiment.
Figure A 3 – IR temperature measurement points and Thermocouple (TC) locations (Cursor 1 and Cursor 2), scale bar in counts.
Figure A 4 – Calibration curve for IR signals obtained from surface of ZT–Cu foam composite through sapphire viewport.