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32nd International Thermal Conductivity Conference
20th International Thermal Expansion Symposium
April 27–May 1, 2014
Purdue University, West Lafayette, Indiana, USA

Metal Hydride Component Design (MHy-CoDe) Tool for the Selection of Hydrides in Thermal Systems

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ABSTRACT

A system has been developed to enable the targeted down-selection of an extensive database of metal hydrides to identify the most promising materials for use in thermal systems. The materials' database contains over 300 metal hydrides with various physical and thermodynamic properties included for each material. Submodels for equilibrium pressure, thermophysical data, and default properties are used to predict the behavior of each material within the given system. The application used at this time is a stationary combined heat and power system containing a high-temperature proton exchange membrane (PEM) fuel cell, a hot water tank, and two metal hydride beds used as a heat pump to increase the efficiency of a natural gas system. The targeted down-selection for this system focuses on the system's coefficient of performance (COP) for each potential pair and the corresponding sensitivity of the COP and has been used to identify the top 20 pairs, with COPs >1.3, for use in this application.

Keywords: metal hydride thermal systems, hydride property database, thermodynamics, metal hydride toolbox, metal hydride heat pump.

1. INTRODUCTION

The use of hydrogen in a high-temperature proton exchange membrane (PEM) fuel cell for stationary combined heat and power (CHP) systems is an active research area (Brew & Glasser, 2005; Chu, 2008; Milestone, 2006; Pollet, 2013 ; Pedrazzi, 2012). In this work, integrating a metal hydride heat pump into a CHP system has been investigated. The goal is to improve the overall efficiency of the CHP system by using hydrogen gas and a pair of tailored metal hydrides to increase the heat recovery of a hot water system. In order to evaluate potential hydrides and enable a targeted down-selection, a metal hydride component design (MHy-CoDe) tool has been developed which builds off the former Sandia hydride database (Hydrogen Storage Materials Database, 2014) and recent work in the literature to identify the most promising metal hydrides for this application. This tool will allow for the identification and ranking of potential hydrides to use in this system using a database of over 300 metal hydrides. For a given heat pump system, this tool provides over 100,000 possible hydride combinations.

The metal hydride heat pump system consists of a pair of metal hydride beds, A and B, through which heat and hydrogen gas are cycled, acting to improve the efficiency of a CHP system with a high temperature PEM fuel cell. A key distinction between this approach and others found in literature is that the mid-temperature hot water reservoir is used to increase heat recovery, rather than applying the system in a refrigeration mode. The interaction between the two hydrides requires the pair to have dissimilar enough thermodynamic properties such that favorable pressure gradients are obtained at the relevant system temperatures. Pairing two unique hydrides makes it possible to use the heat from ambient surroundings as well as the more readily accessible heat from the fuel cell (or reformer) to heat a water reservoir.

The main components of the system include the two metal hydride beds, fuel cell, hot water reservoir, and the surroundings. Heat can be exchanged between components in different directions depending on the hydrogen absorption/desorption cycle. Preliminary calculations using simplified property analysis indicate that this design can result in at least a 20% point increase in system efficiency by increasing the heat recovered to the hot water as long as the heat pump COP is sufficiently high (~1.3). To accurately select hydrides to test in this system, improved pressure-composition isotherm (PCI) models and material specific data, such as weight capacity and thermodynamic values, are required. These models and data are organized into the MHy-CoDe tool. A major focus of this work is to use this database to identify which hydride pairs can meet the COP requirements for this application.

DOI: 10.5703/1288284315541

2. METHODS

Several criteria are required to down-select the 100,000+ pairs in the hydride database to those that can satisfy the system requirements. The database of hydrides must be sufficiently populated with well-known hydrides for which reliable data is available. Screening criteria must be easily modifiable to allow for versatility of this tool. Information and standardized representative models for kinetics and thermodynamics are required for all hydrides being considered. Selection criteria must be easily applied to candidate hydrides to further down-select materials for testing.

In order to meet the above criteria, we developed an object oriented MATLAB Toolbox which incorporates an extensive metal hydride property database and appropriate submodels. The submodels used describe equilibrium pressure, thermophysical properties, and default properties. This toolbox was used in this work to identify potential hydrides for use in the proposed heat pump system, and has been made available online as a freely available software resource (Purdue Metal Hydride Toolbox, 2014).

2.1 Metal Hydride MATLAB Toolbox

The Metal Hydride MATLAB Toolbox provides an object-oriented interface for metal hydride analysis using a built-in database of over 300 metal hydrides along with robust models for thermodynamic, kinetic, and thermophysical hydride properties. The metal hydride objects defined by this tool provide a unified object, containing both data (hydride properties from the database) and methods (application of appropriate property models). This allows us to perform general analysis on a wide range of hydride types while maintaining fidelity to the inherent differences in these hydride types. This is designed to provide a single unified interface for analysis within MATLAB, so calculation of relevant parameters (e.g. ΔH, P_{eq}, reaction rate) can be done generally for any hydride in the database. The design of this database and accompanying models are described in detail in Voskuilen, Waters, and Pourpoint (2014) and are summarized herein.

2.1.1 Property database

The property database component of the toolbox includes over 300 hydrides from about 150 literature references. Every entry in the database contains, at a minimum, the hydride type, alloy composition, reversible hydrogen capacity, and desorption thermodynamics. In addition, each hydride can contain full or partial hydriding thermodynamics, plateau slope, thermophysical properties, and reaction kinetics. Hydriding thermodynamics can be fully defined by any two properties out of the following lists: enthalpy of reaction, entropy of reaction, hysteresis (expressed by $\ln(P_a/P_d)$), or critical temperature.

2.1.2 Equilibrium pressure

It is essential to have a good model for equilibrium pressure to accurately model the dynamic temperature response of a metal hydride reactor. The model requirements for this system are described by Voskuilen et al. (2014). To meet all these criteria, a linear chemical potential in the two-phase region and a regular solution model outside that region are used. This is essentially a sloped P_{eq} model with a limiting function applied only to the tails of the isotherm, which is realistic for many isotherms and still allows a zeroth-order kinetics model that is limited only by equilibrium to be used. The PCI curves for about 30 different hydrides have been obtained and this model is found to be a good representation of the measurements from a range of material types.

2.1.3 Thermophysical models

The effective thermal conductivity and density of the metal hydrides are obtained from the property database when available and a set of default values are accessed when needed. The standard default property set was modified for other types where data was available from the literature. For example, the AB, AB_2, and AB_5 hydride defaults are the average of the reported values currently in the database. As the database becomes more populated, these averages can be updated as-needed.

Since the hydrogen content affects the metal's heat capacity (Flueckiger, 2010; Dadson, 2013; Sonntag & Van Wylen, 1965), the specific heat of each metal hydride is calculated as:

$$C_p(w) = C_{p,M}\left(1 + \frac{H(w)}{M}\right) \tag{1}$$

where $H(w)$ is the number of hydrogen atoms per metal formula unit at the current hydrogen mass fraction, M is the number of metal atoms per formula unit, and $C_{p,M}$ is the heat capacity of the fully dehydrided metal (obtained from the property database). Further discussion regarding the treatment of these parameters can be found in Voskuilen et al. (2014).

2.2 Hydride pair selection

Selection of hydride pairs is done using the Metal Hydride MATLAB Toolbox to consider every possible combination of hydrides for A and B, apply a set of system specific selection criteria, and check whether a given pair is valid for the system. Currently, the set of selection criteria comprised maximum and

minimum system pressures, hydriding efficiency with respect to hydride mass, and coefficient of performance (COP).

For each transfer, there must exist a positive pressure difference between the two beds for the entirety of the hydrogen transfer. For this pressure relationship to be verified, two conditions must be tested. The first condition is that the dehydriding pressure of hydride A at T_{high} must be greater than the hydriding pressure of hydride B at T_{mid}. The second condition is that the dehydriding pressure of hydride B at T_{low} must be higher than the hydriding pressure of hydride A at T_{mid}. The maximum system pressure is set by the desorbing pressure of hydride A at T_{high} and the minimum system pressure is set by the absorbing pressure of hydride A at T_{mid}. A minimum limit for hydriding efficiency can be specified within the selection tool.

Hydriding efficiency is calculated based on the intersection points between the two isotherms of each pair when an isotherm is reversed. These intersections indicate how much hydrogen can be transferred before equilibrium is reached. The shaded regions in Figure 1 indicate the efficiency of the $V_{0.8455}Ti_{0.1045}Fe_{0.05}$ – $Ti_{1.1}Cr_{1.2}Mn_{0.8}$ hydride pair. For this system, efficiency is the fraction of a hydride's total hydrogen capacity that is used in the heat pump cycle.

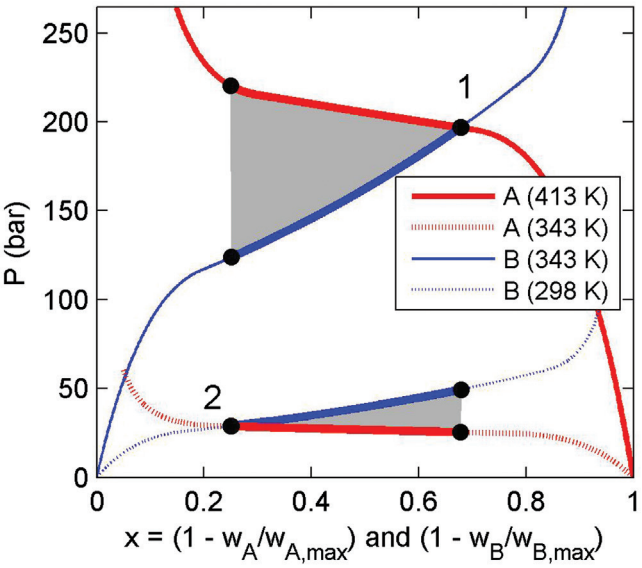

Figure 1. Hydriding/dehydriding cycle for $V_{0.8455}Ti_{0.1045}Fe_{0.05}$ – $Ti_{1.1}Cr_{1.2}Mn_{0.8}$.

Hydriding mass efficiency is defined as

$$\eta = x_1 - x_2 \tag{2}$$

where x_1 and x_2 correspond to points 1 and 2 in Figure 1, respectively.

A useful metric for measuring the performance of each pair is the system's COP. The COP is defined as the ratio of the heat from the hot water to the heat from the fuel cell. For pairs with a COP <1, the heat pump is a detrimental addition to the system and thus pairs with such COP values are not considered to be valid. The COP for a given hydride pair is defined as:

$$\mathrm{COP} = \frac{\eta\left(\left|\Delta H_{A,abs}\right| + \left|\Delta H_{B,abs}\right|\right) + L_A - L_B}{\eta\left|\Delta H_{A,des}\right| + L_A} \tag{3}$$

where the latent heats are given by:

$$L_A = \frac{C_{p,A}}{W_{max,A}}(T_{high} - T_{mid}) \tag{4}$$

$$L_B = \frac{C_{p,B}}{W_{max,B}}(T_{mid} - T_{low}) \tag{5}$$

A given hydride pair may have a high calculated COP, but if the pressure difference between the hydrides during transfer is low, its achievable COP will be very sensitive to the actual thermodynamics of the hydrides.

In order to down-select our list of valid hydrides, a calculation for the sensitivity of the calculated COP to variations in the input hydride properties is added. Some hydrides considered have only enthalpy and entropy values, whereas others have full isotherms. To quantify the potential effect of these differences, uncertainties to the inputs from the hydride database are assigned, and several approaches for propagating these uncertainties through to the final calculated COP are investigated.

All hydrides in the database have desorption thermodynamic data, and therefore the uncertainty on those values is set at 2% based on standard reported values in the literature. The uncertainty for the absorption thermodynamic parameters is varied depending on their "thermo level", which is the number of thermodynamic parameters obtained from the literature for that hydride's absorption. The uncertainties corresponding to thermo levels 0, 1, and 2 are 6%, 4%, and 2%, respectively.

The slope is stored in the database as:

$$\mathrm{Slope} = \left.\frac{\partial(\ln(P))}{\partial x}\right]_{x=0.5} \tag{6}$$

The uncertainty in the plateau slope is set as 0.5 if no slope is available from the literature (based on statistical analysis of the existing hydride database) or 0.05 if the slope is available from the literature. These uncertainties are used with two different thermodynamic models, described later, to assess the sensitivity of the calculated COP.

The Nishizaki model is a useful way of modeling the equilibrium pressure of acceptable pairs with a simple analytical function. The inputs to this model are enthalpy, entropy, and slope. The equation given by the Nishizaki model to relate pressure, temperature, and thermodynamic values is:

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} + \frac{\text{slope}}{\pi}\tan(\pi(x - 0.5)) \tag{7}$$

Using the Nishizaki model for the equilibrium pressure, x_1 and x_2 in Equation (2) are defined as

$$x_1 = \frac{1}{\pi}\tan^{-1}\left[\frac{\pi}{\text{slope}_A + \text{slope}_B}\left(\frac{\Delta H_{A,d}}{T_{high}R} - \frac{\Delta H_{B,a}}{T_{mid}R} + \frac{S_{B,a}}{R} - \frac{S_{A,d}}{R}\right)\right] + \frac{1}{2} \tag{8}$$

$$x_2 = \frac{1}{\pi}\tan^{-1}\left[\frac{\pi}{\text{slope}_A + \text{slope}_B}\left(\frac{\Delta H_{A,a}}{T_{mid}R} - \frac{\Delta H_{B,d}}{T_{low}R} + \frac{S_{B,d}}{R} - \frac{S_{A,a}}{R}\right)\right] + \frac{1}{2} \tag{9}$$

Although the Nishizaki model is a simplification of the actual behavior, the results are comparable and those achieved using this model serve to corroborate and validate the results from the built-in thermodynamic model. Figure 2 shows a comparison of the equilibrium pressure between the two models, illustrated using pair $V_{0.8455}Ti_{0.1045}Fe_{0.05} - Ti_{1.1}Cr_{1.2}Mn_{0.8}$.

It is most important to have model agreement between the two intersection points, where the hydrogen transfer between material beds will occur. As demonstrated in Figure 2, the two models are sufficiently equivalent to justify the use of the Nishizaki model to determine COP sensitivity by propagating the error throughout COP calculation. However, the example case shows a hydride with non-zero slope so that the behavior will differ for some hydride pairs. The uncertainty in the COP can be calculated by:

$$e_{COP}^2 = \sum_i \left(\frac{\partial \text{COP}}{\partial x_i} e_{x_i}\right)^2 \tag{10}$$

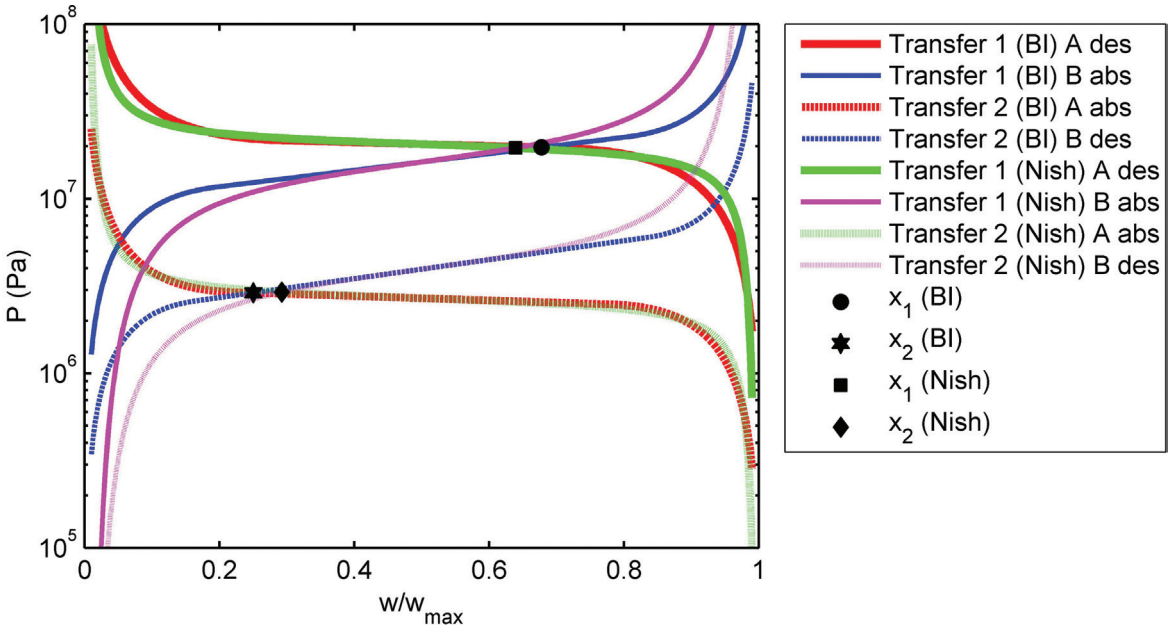

Figure 2. Nishizaki and built-in thermodynamic models comparison using $V_{0.8455}Ti_{0.1045}Fe_{0.05} - Ti_{1.1}Cr_{1.2}Mn_{0.8}$.

Sensitivities for each parameter are reported as the fractional sensitivity, defined by:

$$f_i = \frac{\left(\frac{\partial \mathrm{COP}}{\partial x_i} e_{x_i}\right)^2}{e_{\mathrm{COP}^2}} \tag{11}$$

where we consider $x_i = \Delta H_{A,a}$, $\Delta H_{A,d}$, $\Delta H_{B,a}$, $\Delta H_{B,d}$, $\Delta S_{A,a}$, $\Delta S_{A,d}$, $\Delta S_{B,a}$, $\Delta S_{B,d}$, slope A, and slope B.

COP sensitivity is a measure of the confidence in the calculated COP for a given metal hydride pair. A high COP sensitivity does not mean that the pair will be better or worse than one with a lower COP sensitivity, merely that if a higher sensitivity pair is chosen, more material analysis will have to be done to verify the data on record for that hydride.

To calculate the COP and COP sensitivity using the built-in thermodynamic model, we use the numerical derivative of COP with respect to the earlier-listed 10 inputs. This numerical approach can be used with the Nishizaki model to illustrate the differences between the two models and to ensure that our results are not highly dependent on which isotherm model to be used.

3. RESULTS AND DISCUSSION

Using minimum and maximum system pressures of 2 and 350 bar, respectively, a minimum efficiency of 30%, and a minimum COP of 1, the distribution of resulting COP values and the number of acceptable pairs for each combination of hydride types are shown in Figure 3. Misc and SS stand for miscellaneous and solid solution hydrides, respectively.

The bar diagram on the right of Figure 3 shows the distribution of valid pairs over all the possible combinations of A and B types. The most common valid types for hydride A are shown to be A_2B_7, AB_2, and AB_5 while those for hydride B are AB_2 and AB_5. Different hydride types are better for use in different beds. For example, A_2B_7 is a good material for hydride A but not for hydride B. The two peaks at AB_5–AB_2 and AB_5–AB_5 are significantly higher than the rest of the peaks because of the higher population of those material types in the database. These materials have been studied extensively for hydrogen storage systems.

To identify the most promising pairs, the calculated COP sensitivity is subtracted from the calculated COP, focusing on the pairs with the highest values of COP – e_{COP}. Table 1 shows the pairs with the highest values of COP – e_{COP} using the built-in thermodynamics model. For each pair, the parameter A/B contribution shows the percentage of total COP sensitivity that is derived from each hydride. This parameter will help to direct the focus toward the most uncertain hydrides within these top 20 pairs. The thermodynamic values of the most uncertain hydrides will be tested first. Materials that appear in multiple high-ranking combinations are particularly preferred because less property validation will be required across those combinations. These hydrides are shown in bold format. For hydride A, the top hydrides of interest include NaAl, Y_2Co_7, and $V_{0.8455}Ti_{0.1045}Fe_{0.05}$, all of which appear in multiple pairs. Of these hydrides, only NaAl has been extensively studied in the literature. For hydride B, there are several VCr alloys, Mm AB_5 alloys, and TiCrMn alloys.

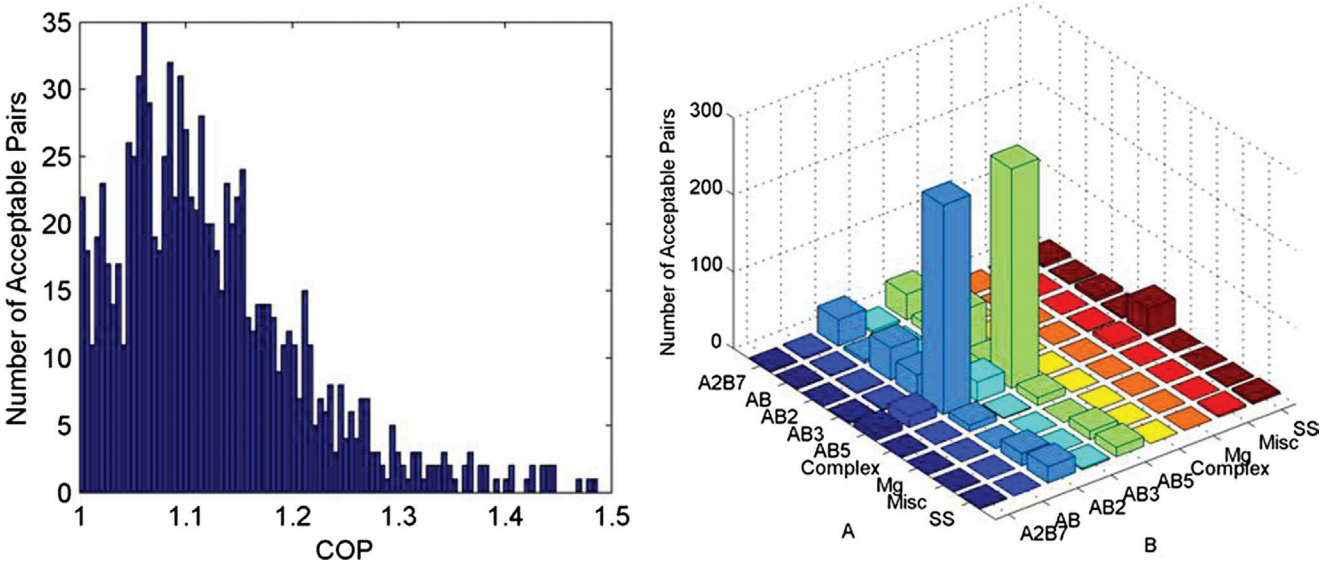

Figure 3. COP distribution for all acceptable pairs (left) and number of acceptable pairs for each combination of hydride types (right).

Table 1. Top 20 pairs according to COP – e_{COP} calculated using the built-in thermodynamic model.

	A	B	COP	e_{COP}	A/B contribution
1	Tb_2Co_7	**$V_{0.95}Cr_{0.05}$**	1.52	0.12	62/38
2	Ho_2Co_7	**$V_{0.9}Cr_{0.1}$**	1.47	0.12	42/58
3	**$V_{0.8455}Ti_{0.1045}Fe_{0.05}$**	**$MmNi_{4.6}Fe_{0.4}$**	1.45	0.10	88/12
4	**NaAl**	$LuCo_3$	1.47	0.15	63/37
5	$La_{0.65}Ce_{0.28}Pr_{0.07}Co_5$	**$V_{0.95}Cr_{0.05}$**	1.44	0.14	39/61
6	**NaAl**	$NdNi_{4.8}Sn_{0.2}$	1.43	0.13	89/11
7	**$V_{0.8455}Ti_{0.1045}Fe_{0.05}$**	**$V_{0.855}Cr_{0.145}$**	1.39	0.09	73/27
8	**NaAl**	**$Mm_{0.5}Ca_{0.5}Ni_5$**	1.47	0.18	83/17
9	$HoCo_3$	Er_2Co_7	1.38	0.10	50/50
10	**NaAl**	$YNi_{4.25}Al_{0.75}$	1.38	0.11	73/27
11	$LaNi_5$	$ErNi_3$	1.35	0.08	25/75
12	**NaAl**	**$MmNi_{4.5}Si_{0.5}$**	1.42	0.16	60/40
13	**Y_2Co_7**	Er_2Co_7	1.34	0.09	67/33
14	**$V_{0.8455}Ti_{0.1045}Fe_{0.05}$**	**$Ti_{1.2}Cr_{1.2}Mn_{0.8}$**	1.36	0.12	56/44
15	**NaAl**	**$MmNi_{3.5}Cu_{0.5}$**	1.36	0.11	79/21
16	**$V_{0.8455}Ti_{0.1045}Fe_{0.05}$**	**$Ti_{1.1}Cr_{1.2}Mn_{0.8}$**	1.32	0.09	75/25
17	**NaAl**	**$Ti_{0.8}Zr_{0.2}Mn_{1.5}Cr_{0.5}$**	1.40	0.17	49/51
18	**Y_2Co_7**	$Zr_{0.76}Ti_{0.24}Ni_{1.16}Mn_{0.63}V_{0.14}Fe_{0.18}$	1.33	0.10	65/35
19	**$V_{0.8455}Ti_{0.1045}Fe_{0.05}$**	**$Ti_{1.2}CrMn$**	1.34	0.11	93/7
20	**$V_{0.8455}Ti_{0.1045}Fe_{0.05}$**	$DyNi_{4.5}Al_{0.5}$	1.33	0.10	78/22

Note: Hydrides of interest are shown in bold.

4. CONCLUSIONS

The MHy-CoDe tool discussed here is a powerful tool for the targeted material selection of metal hydrides in thermal systems. This capability of identifying hydride pairs for use in a metal hydride heat pump as part of a CHP system has been used. The goal is to identify metal hydride pairs with a high enough COP (~1.3) to increase the net efficiency of the system. To identify such pairs, a material database containing more than 300 metal hydrides is assembled. This database population results in over 100,000 possible hydride combinations.

The results obtained to date have shown important trends and relationships between hydride pair properties and overall system behaviors. By analyzing a large set of potential hydrides, numerous high COP and high efficiency pairs for further investigation have been identified. Out of the more than 100,000 pairs, an informed selection was made of the top 20 highest performing pairs. As shown in this work, the top 20 hydrides have COPs > 1.3. Of the hydrides with COPs > 1, the average COP is ~1.1.

To provide additional confidence in the metal hydrides selected for experimental characterization, a COP sensitivity parameter is defined to reflect the reliability and state-of-knowledge of the metal hydride properties in the database. As such, the COP sensitivity parameter, along with the corresponding COP values, serves to guide us in selecting a subset of metal hydrides to focus our experimental characterization on.

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