

Thermal behavior of solid acids in the $\text{Rb}_3\text{H}(\text{SO}_4)_2\text{-RbHSO}_4$ system under ambient atmosphere

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Abstract

The thermal behavior of solid acids in the $\text{Rb}_3\text{H}(\text{SO}_4)_2\text{-RbHSO}_4$ system under ambient atmosphere has been studied in comparison to the previously reported high-temperature behavior of the same system under humidified atmosphere. The findings showed that, under this level of humidity, the transition of RbHSO_4 , the transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$, and the disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, occurred at the same temperatures as those under humidified atmosphere. However, the results from differential scanning calorimetry did not reveal the reaction temperature between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 due to the slow process. The dehydration temperatures of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ were surprisingly similar between the systems under low and high humidity levels, while the dehydration of RbHSO_4 under low humidity occurred at a lower temperature than that previously reported. Additionally, the findings suggested that the humidity levels played some roles in the kinetics of the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 which should be further studied.

1. Introduction

A solid acid is a salt product of a regular acid-base or an ion-exchange reaction between a polyprotic acid, such as H_2SO_4 or H_2SeO_4 , and a base or a salt, such as Cs_2CO_3 or Cs_2SO_4 , and must have at least one acidic proton remains in the salt unit structure. The general formula of solid acids can be written as $\text{M}_p\text{H}_q(\text{XO}_4)_r$ where usually $\text{M} = \text{Cs}$, Rb , K , NH_4 ; $\text{X} = \text{S}$, Se , P ; and $(p+q)/2 = r$ and the same pair of the acid and the base can produce different solid acid compounds, for example RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$, depending on the mole ratios chosen in the reactions. Combinations of these cations or anions at various mole ratios can also give new solid acids in forms of solid solutions with more complex structures [1-5] and alter their thermal and electrical behaviors [4-6], for instance $(\text{Cs}_x\text{Rb}_{1-x})_3\text{H}(\text{SeO}_4)_2$, which will allow more flexibility to utilize this class of materials. Many solid acids undergo polymorphic superprotonic phase transition, giving the increase in conductivity by 3-4 orders of magnitude, at relatively lower temperatures, $\sim 100^\circ\text{C}$ to 300°C [4-20]. This fact draws attention from researchers to utilize solid acids as proton-conductors, ultimately in applications like fuel cells or electrolyzers [21,22]. In solid acid fuel cells as depicted in Figure 1, solid acids are used as the electrolytes which also separate the fuel and the oxidant gases from each other. The fuel, like pure hydrogen gas, is fed into the anode side without water vapor to keep the fuel concentration and the cell voltage high, while the oxidant, like air or oxygen gas, is fed into the cathode side along with a controlled water partial pressure to maintain a stable voltage of the fuel cell. The two sides of the same electrolytes thus expose to different atmospheres. Hence, the understanding of the material behaviors under the different humidity levels is necessary.

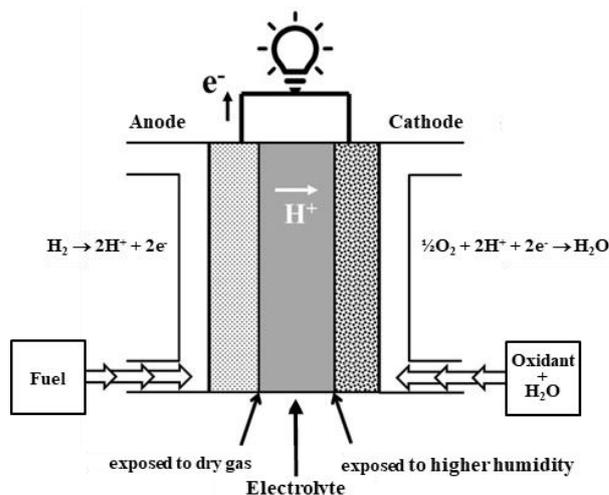


Figure 1. Schematic diagram of a solid acid fuel cell.

Dehydration is another property of solid acids that limits the operating temperature in applications. As described above, solid acids have high conductivity at temperatures above the superprotonic phase transition, but the dehydration can also take place from 200°C to 300°C depending on the solid acids and the water partial pressure in the atmosphere [6,9-11,23-25]. Generally, the more water in the atmosphere, the higher the dehydration temperature [6,9,23,24]. Furthermore, the dehydration of solid acids usually involves a liquid phase, so they would fail as a solid electrolyte. Therefore, it is also necessary to study the dehydration behavior of solid acids to avoid the failure, especially under the low humidity.

$\text{Rb}_3\text{H}(\text{SO}_4)_2$ is a solid acid which presents an increase in conductivity at 203°C, similar to other solid acids. What is different is that the origin of this higher conductivity is not from the simple phase transition of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, but comes from one of the disproportionation products of this compound, $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$, which has higher conductivity by its nature [24,26]. The $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ can also form at even lower temperatures if $\text{Rb}_3\text{H}(\text{SO}_4)_2$ is present along with RbHSO_4 as demonstrated in another study [26]. The two compounds react with each other at a temperature below 140°C and give the less conductive, lower temperature (LT) phase of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ before it transforms to the more conductive, higher temperature (HT) phase at 185°C, which evidently the same phase as the disproportionation product of $\text{Rb}_3\text{H}(\text{SO}_4)_2$. Another noteworthy result from the previous report is that the conductivity of the LT- $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ was already much higher than the two original compounds, by 2-3 orders of magnitude even at 140°C, the lowest temperature examined. This suggests the potential of utilizing this compound at lower temperatures while the conductivity is still high enough.

The main goal of this work was to study the thermal behavior of the mixtures between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 under the relatively low humidity level of the ambient air. The reactions of interest in this work included the transition of RbHSO_4 , the transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$, the disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, and the dehydration of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$, which were previously studied under only high humidity level [24,26] and had not been carried out in low humidity. The temperature of the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 , which had never been reported before, was also inspected in the same measurements along with the other reactions above.

2. Experimental methods

2.1 Sample preparation

Both RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ were prepared from aqueous solutions of Rb_2SO_4 (99% metal basis, Alfa Aesar) and H_2SO_4 (95-97%, EMSURE) with different $\text{Rb}_2\text{SO}_4 : \text{H}_2\text{SO}_4$ molar ratios which were 1 : 2 for RbHSO_4 and 3 : 1 for $\text{Rb}_3\text{H}(\text{SO}_4)_2$. The solution for RbHSO_4 was then left to crystallize before the crystals were removed from the solution and rinsed with water and acetone sequentially. The crystals were then ground, dried at about 100°C overnight in a drying oven. The solution for $\text{Rb}_3\text{H}(\text{SO}_4)_2$ was poured into methanol to induce precipitation. The white powder of the product was filtered and washed with methanol before it was dried the same way as the RbHSO_4 crystals were. The mixtures of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 with 0, 20, 66.67, 80, and 100% mole RbHSO_4 were prepared by simple mixing and grinding in a mortar. All samples were kept in a desiccator with silica gel as the desiccant until further examinations. The humidity inside the desiccator, measured using a DAIHAN A1.H9213 hygro-thermometer and even though not continuously monitored, was translated to $P_{\text{H}_2\text{O}} \sim 0.007$ atm at most.

2.2 X-ray diffraction (XRD)

A Bruker D8 Advance x-ray diffractometer with Cu K_α radiation was employed for the XRD measurements. The measurements were performed using 0.02-degree step size and 1-s per step in the 2θ range

of 10 to 60 degrees. The products from the syntheses of RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ were confirmed by XRD measurements prior to further experiments. The 66.67%- RbHSO_4 mixture samples after the heat treatment at 140°C for 2 h under ambient humidity ($P_{\text{H}_2\text{O}} \sim 0.006$ atm) in stagnant air were also studied the phases using the same settings.

2.3 Thermal analysis

The differential scanning calorimetry (DSC) and the thermogravimetric analysis (TGA) were carried out using a LINSEIS STA PT1600. The samples, 60-80 mg each, were compressed into 5-mm pellets for better heat transfer. The measurements were done under ambient humidity ($P_{\text{H}_2\text{O}} \sim 0.006$ atm) in stagnant air and the temperature range was from room temperature to 300°C with a heating rate of $2^\circ\text{C}\cdot\text{min}^{-1}$, then the temperature was held constant for 30 min before cooling to room temperature with a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$. An additional setting for the 66.67%- RbHSO_4 sample was executed with an extra dwelling step at 140°C for 2 h on heating to demonstrate the kinetics of the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 . The ambient relative humidity and the temperature near the DSC chamber were measured at the beginning, during, and at the end of the measurements using the same equipment used to measure the humidity inside the desiccator.

3. Results and discussion

The results from the thermal analysis under low humidity of RbHSO_4 , $\text{Rb}_3\text{H}(\text{SO}_4)_2$, the 66.67%- RbHSO_4 sample, and the 66.67%- RbHSO_4 sample with the dwelling step are shown in Figure 2(a)-2(d), respectively. The thermogram of RbHSO_4 in Figure 2(a) exhibits a strong endothermic signal corresponding to the weight loss from dehydration at 205.7°C, a little lower than the value from thermo-mechanical analysis, 213°C, under similar humidity level reported previously [24].

The disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ occurred at 201.6°C, as can be seen in Figure 2(b), also not much different from 205°C published earlier [24,26]. Even though a weight loss was observed in the TG measurement of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ at about 250°C, there was no observable peak in the DSC profile at that temperature, possibly due to the weight change percentage was small (~1%). Additionally, the fact that the dehydration temperature here was not different from the temperature reported in the publications by Cowan *et al.* [24] and Panithipongwut *et al.* [26], even though the water partial pressures were different, is somewhat surprising because water is one of the products in the dehydration reaction and its content in the atmosphere usually alters the dehydration temperatures in the other solid acid systems [6,23]. Also, it should be noted that this weight loss came from the dehydration of one of the disproportionation products, HT- $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$, not the dehydration of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ itself, as documented in the same publications.

Figure 2(c) and 2(d) display the results of the same mixture sample, 66.67%- RbHSO_4 composition, under the same atmosphere, but were measured with different temperature profiles. The former was examined without a soaking step, while the latter was studied with a constant-temperature step at 140°C for 2 h. As Panithipongwut *et al.* presented already, $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 reacted stoichiometrically

and completely at this composition at a temperature below 140°C under humidified atmosphere [26] and this behavior was demonstrated by the single endothermic peak at 185°C , corresponding to the phase transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$. However, under this drier condition, there were three signals detected at about 170 , 182 , and 202°C , corresponding to the transition of RbHSO_4 , the transition of $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$, and the disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, respectively. The endothermic peak at 182°C hinted that the $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ was formed before reaching this temperature, similar to what happened in the humidified system, although no other peak was observed below 140°C . The peak at 202°C in both figures, however, revealed that there was a portion of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ remained in the mixture and the reaction between RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ was not completed and the small endothermic peak at 170°C , ascribed to the phase transition of RbHSO_4 , confirmed that. This suggested that the reaction between the two reactants under humidified atmosphere proceeded much faster than under dry atmosphere. It should also be noted that these three reactions under the low humidity occurred at the temperatures which agreed well with those of the reactions in the humidified gas [24]. This means that the water vapor pressure, as expected, does not affect the reaction temperatures of these reactions.

Upon heating to higher temperatures, both of the 66.67%- RbHSO_4 samples dehydrated around 250°C as indicated by the weight loss, without a clear associating peak in the heat flow plot, similar to the pure $\text{Rb}_3\text{H}(\text{SO}_4)_2$ sample. Again, the phase that dehydrated here was $\text{HT-Rb}_5\text{H}_3(\text{SO}_4)_4$. The physical appearances of these samples after cooled down to the room temperature were glossy and dense, giving a hint of having melted or transformed into a liquid state when they were heated to above the dehydration temperature. These behaviors happened in the thermal analysis measurements of the other compositions as well and were similar to what described by Cowan *et al.* [24]. The reaction temperatures and the corresponding reaction enthalpies of all samples were summarized in Table 1 and Table 2, respectively. The data in Table 1 shows that all reactions involved in this system occurred in the same range across the compositions. It should be noticed too that the dehydration temperature of the pure RbHSO_4 was very close to the disproportionation temperature of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, which led to a plausible overlapping of the two peaks and resulted in apparent higher enthalpy values of the peak at this temperature as shown in Table 2, especially for the compositions with higher amounts of RbHSO_4 , at which the enthalpy increased dramatically, for example, that of the 80% RbHSO_4 composition.

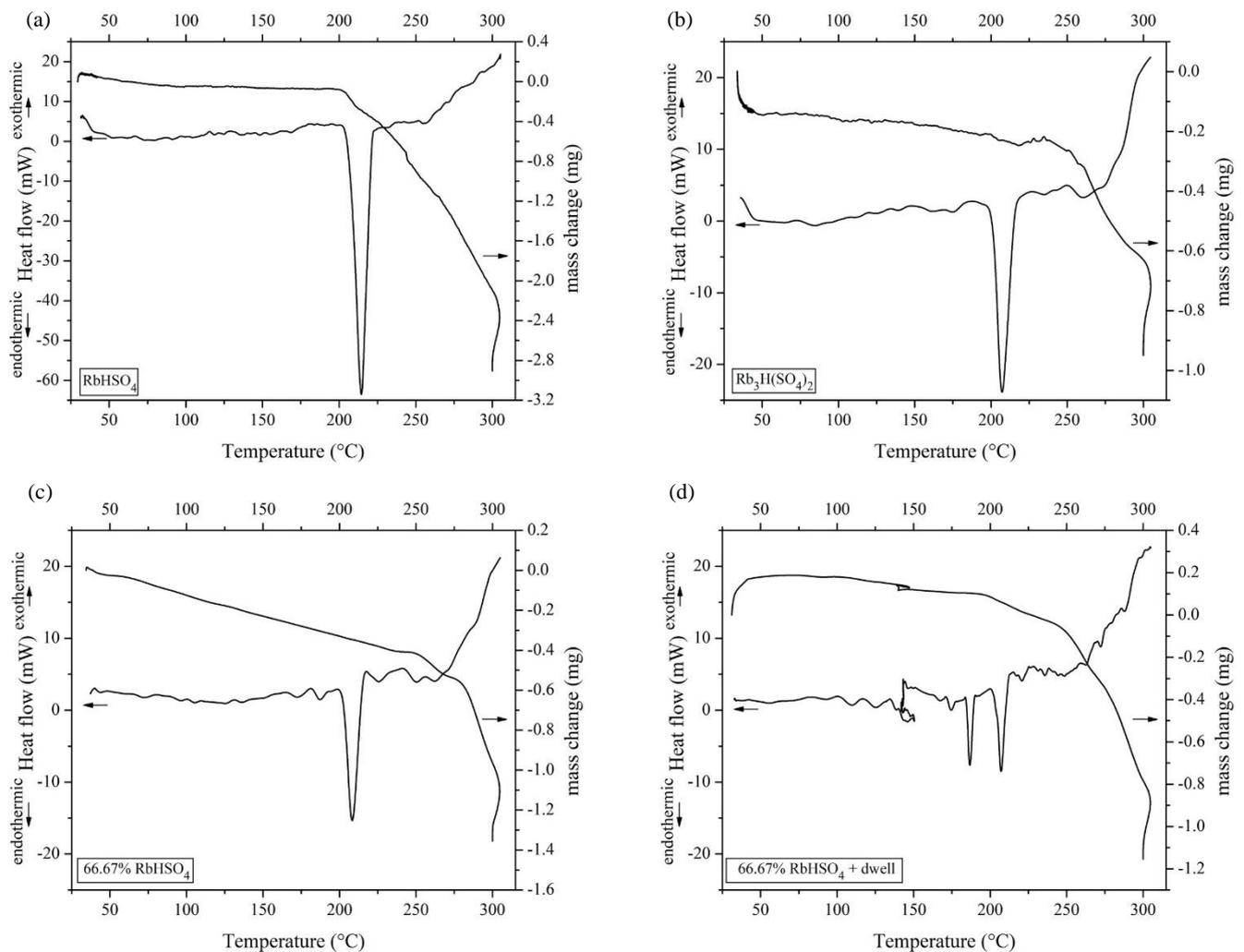


Figure 2. DSC and TG profiles under ambient humidity ($P_{\text{H}_2\text{O}} \sim 0.006$ atm) of (a) RbHSO_4 , (b) $\text{Rb}_3\text{H}(\text{SO}_4)_2$, (c) the 66.67%- RbHSO_4 sample, and (d) the same composition with a dwelling step at 140°C for 2 h. The ramp rate for all measurements was $2^\circ\text{C}\cdot\text{min}^{-1}$.

Table 1. Temperatures of reactions in the $\text{Rb}_3\text{H}(\text{SO}_4)_2$ - RbHSO_4 system at various compositions. The exact temperature of the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 is still undetermined.

RbHSO ₄ :Rb ₃ H(SO ₄) ₂ ratio	Reaction temperatures (°C)			
	Transition of RbHSO ₄	Transition of Rb ₅ H ₃ (SO ₄) ₄	Disproportionation of Rb ₃ H(SO ₄) ₂	Dehydration
0:100	–	–	201.6	250.4
20:80	170.4	181.7	202.7	251.4
60:40	165.2	183.5	201.8	243.6
66.67:33.33	170.3	182.3	202.5	253.0
80:20	170.0	182.5	203.0	243.9
100:0	UD	–	–	205.7

UD = expected, but undetectable. – = no such reaction in the sample

Table 2. Enthalpies of reactions in the $\text{Rb}_3\text{H}(\text{SO}_4)_2$ - RbHSO_4 system at various compositions.

RbHSO ₄ :Rb ₃ H(SO ₄) ₂ ratio	Enthalpy of reaction (J·g ⁻¹)			
	Transition of RbHSO ₄	Transition of Rb ₅ H ₃ (SO ₄) ₄	Disproportionation of Rb ₃ H(SO ₄) ₂	Dehydration
0:100	–	–	-62.00	(b)
20:80	-0.78	-2.39	-59.08	(b)
60:40	-0.96	-2.86	-65.10	(b)
66.67:33.33	-1.11	-6.31	-70.02	(b)
80:20	-2.47	-4.89	-108.47	(b)
100:0	UD	–	–	-169.02

UD = expected, but undetectable. – = no such reaction in the sample. ^(a) The enthalpy values at this temperature for the compositions with high content of RbHSO_4 might be combinations of the energies of the disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and that of dehydration of RbHSO_4 . ^(b) Unable to integrate the peak area.**Table 3.** Enthalpies of reactions of the 66.67%- RbHSO_4 samples without and with a soaking step under low humidity. The enthalpy of transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ under humidified atmosphere is $23.8 \text{ kJ}\cdot\text{mol}^{-1}$ ($29.2 \text{ J}\cdot\text{g}^{-1}$) as reported in [7].

Soaking step	Enthalpy of reaction (J·g ⁻¹)		
	Transition of RbHSO ₄	Transition of Rb ₅ H ₃ (SO ₄) ₄	Disproportionation of Rb ₃ H(SO ₄) ₂
None	-1.11	-6.31	-70.02
140°C, 2 h	-1.45	-12.79	-38.20

The differences between the findings in Figure 2(c) and 2(d) were the intensities of the three endothermic peaks mentioned above. In Figure 2(c), the first two peaks were quite weak, and the third peak was still quite high, compared to that of the pure $\text{Rb}_3\text{H}(\text{SO}_4)_2$. The intensities of the second and the third signals changed noticeably in Figure 2(d), while that of the first was still low. The comparison of the DSC profiles of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and of the 66.67%- RbHSO_4 sample without and with the dwelling step is shown in Figure 3. The enthalpy values of the reactions extracted from the DSC measurements without and with the soaking step were listed in Table 3. The enthalpy associating with the transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ in the 66.67%- RbHSO_4 sample without the dwelling step was $6.31 \text{ J}\cdot\text{g}^{-1}$, which was much smaller than the one under humidified condition, $29.2 \text{ J}\cdot\text{g}^{-1}$, previously reported [7]. This is another evidence that the reaction between RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ was incomplete. The other experimental trial with the soaking step revealed that, by doing so, the transition enthalpy of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ increased to $12.79 \text{ J}\cdot\text{g}^{-1}$, implying more LT- $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ produced at a lower temperature, yet still lower than that in humidified atmosphere, while that of RbHSO_4 was about the same (1.11 and $1.45 \text{ J}\cdot\text{g}^{-1}$, respectively) and the disproportionation enthalpy of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ decreased dramatically from $70.02 \text{ J}\cdot\text{g}^{-1}$ to $38.20 \text{ J}\cdot\text{g}^{-1}$. This means that the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 is slow and requires a longer time to complete under the low humidity, while in the

humidified case, the reaction was complete in shorter times, as short as 30 min [26]. The preliminary experiments for soaking times of 4 h and 6 h at 140°C were also conducted. As the soaking time increased, the enthalpy of the transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ increased, while those of the transition of RbHSO_4 and the disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ decreased to almost undetectable values. This suggested that the reaction between RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ under low humidity required about 6 h to complete. This also might be the cause of the absence of the signal of the reaction between RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ in the DSC measurement, i.e., the amount of heat involved in the reaction was spread over a wide temperature range and became undetectable. The water content in the atmosphere seemed to facilitate the reaction here as RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ are both solids and the solid-solid reaction usually requires higher temperatures to overcome the high activation energy of the diffusions in solids. In the case of solid acids, however, Sakashita *et al.* [27] described the effect of water on the proton transport mechanism in $\text{Cs}_5\text{H}_3(\text{SO}_4)_4\cdot x\text{H}_2\text{O}$. The presence of the crystalline water weakened the interactions between pairs of the SO_4 tetrahedra and allowed them to reorient faster, and hence increased the proton transport rate. A similar mechanism might occur here, i.e., the water molecules in the atmosphere could be absorbed by the solid acids, which are slightly hygroscopic by their natures, and allowed the ions in RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ to rearrange

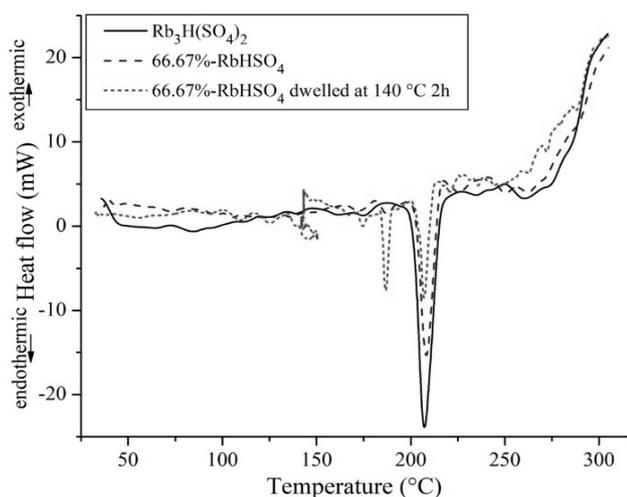


Figure 3. Comparison of the DSC profiles under ambient humidity ($P_{\text{H}_2\text{O}} \sim 0.006$ atm) of $\text{Rb}_3\text{H}(\text{SO}_4)_2$, the 66.67%- RbHSO_4 sample, and the same composition with a dwelling step at 140°C for 2 h. The ramp rate for all measurements was $2^\circ\text{C}\cdot\text{min}^{-1}$.

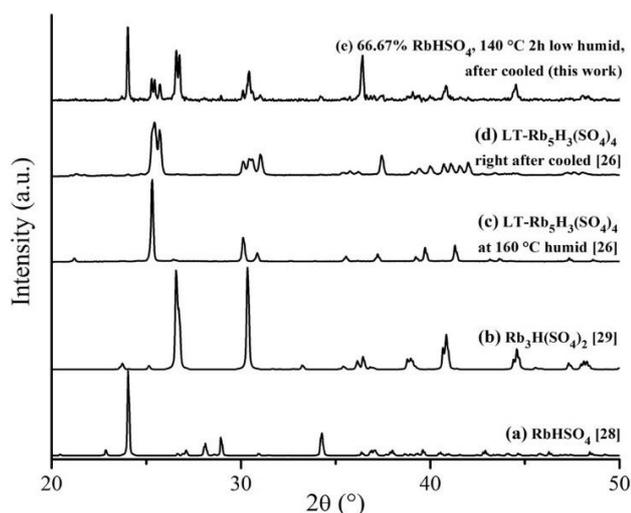


Figure 4. XRD patterns of (a) RbHSO_4 [28], (b) $\text{Rb}_3\text{H}(\text{SO}_4)_2$ [29], (c) $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ measured in-situ at 160°C under humidified ($P_{\text{H}_2\text{O}} \sim 0.032$ atm) atmosphere [26], (d) $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ immediately after cooled to room temperature before phase separation into RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ [26], and (e) the 66.67%- RbHSO_4 sample after heated at 140°C for 2 h in stagnant air ($P_{\text{H}_2\text{O}} \sim 0.006$ atm) and cooled to room temperature (this work).

themselves, or even diffuse, and form new bonds, resulted in the product, $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$, faster. This would explain the different kinetic behaviors of the reaction under the two atmospheres. More experiments are being conducted to confirm and to learn how long it takes to complete the reaction in different conditions in addition to determining the exact reaction temperature. The sample with the dwelling step was also examined via XRD technique after cooled to the room temperature to confirm that the $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ could be formed at a temperature below 140°C under low humidity condition. In this experiment, the 66.67%- RbHSO_4 sample was heated up to only 140°C and the temperature was held constant for 2 h before cooled down to room temperature. The sample was taken to the XRD measurement shortly afterwards. The XRD pattern of this sample is shown in Figure 4, along with the patterns

of RbHSO_4 [28], $\text{Rb}_3\text{H}(\text{SO}_4)_2$ [29], $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ measured in-situ at 160°C [26], and $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ measured immediately after cooled to room temperature before phase separation into RbHSO_4 and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ [26]. It can be seen from Figure 4(d) that $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$, although not stable at room temperature, does not instantly undergo phase separation when cooled to room temperature. Its XRD pattern still retains a combination of diffraction signals from the phase at 160°C and room temperature phases and it will take several days before $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ completely transforms back to the two room-temperature phases. This behavior can help validate the formation of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$. The fact that the pattern of the current sample (Figure 4(e)) matched with characteristic peaks in Figure 4(a) - 4(d), $2\theta \sim 24$ - 31 degrees, indicates that under low humidity, $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ could partially form and the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 was not complete as of holding the temperature at 140°C for 2 h. This confirmation from the XRD experiment agrees well with the results from the thermal analysis.

4. Conclusions

The transition of RbHSO_4 , the transition of $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$, and the disproportionation of $\text{Rb}_3\text{H}(\text{SO}_4)_2$ of the mixtures in low humidity occurred at the temperatures around 170 , 182 , and 202°C , respectively, which agreed well with those of the reactions in humidified gas [24]. This means that the water vapor pressure does not affect these reactions as expected. The onset temperature of the dehydration of $\text{HT-Rb}_5\text{H}_3(\text{SO}_4)_4$ was observed in the range of 243.6 - 253.0°C across the compositions, about the same as the reported temperature for $\text{Rb}_3\text{H}(\text{SO}_4)_2$ after its disproportionation [24,26] even though the water partial pressures were different, which was somewhat unexpected. The onset of the dehydration temperature of RbHSO_4 in this condition was at 205.7°C , slightly lower than that previously reported, 213°C [24]. No peak of the reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 was observed. However, the fact that the signal of the phase transition of $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ appeared around 181.7 - 183.5°C , consistent with the results of the system under the humidified atmosphere, indicated that $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 must react and form $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ already at a lower temperature, but the reaction was incomplete as can be seen from the low transition enthalpy of $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$, in addition to the presences of the peaks of the reactions of the two individual reactants. Holding the temperature at 140°C for 2 h increased the amount of $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ formed, yet the reaction was still not complete. These results pointed out the slow reaction between $\text{Rb}_3\text{H}(\text{SO}_4)_2$ and RbHSO_4 , and a longer time, possibly up to 6 h, was required for the reaction to complete under the low humidity condition. The water content in the gas phase must play some roles in the reaction between them and the mechanism of the reaction involving water vapor is interesting for future investigations. Thus, if this solid acid system is adopted as the electrolyte in fuel cells, it is likely that its properties will not be uniform, and the overall conductivity will be somewhat lower than expected due to the fact that $\text{Rb}_5\text{H}_3(\text{SO}_4)_4$ is not entirely formed, especially during the first couple of hours after the cell starts, which is not ideal for practical uses. On the other hand, the slow transformation might be useful if ones want to retain the $\text{LT-Rb}_5\text{H}_3(\text{SO}_4)_4$ phase to a lower temperature for a longer time, which will allow for high conductivity at lower operating temperatures. This behavior is also of interest for the future study.

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