The Dehydration Behavior of a CsH_2PO_4 Superprotonic Conductor

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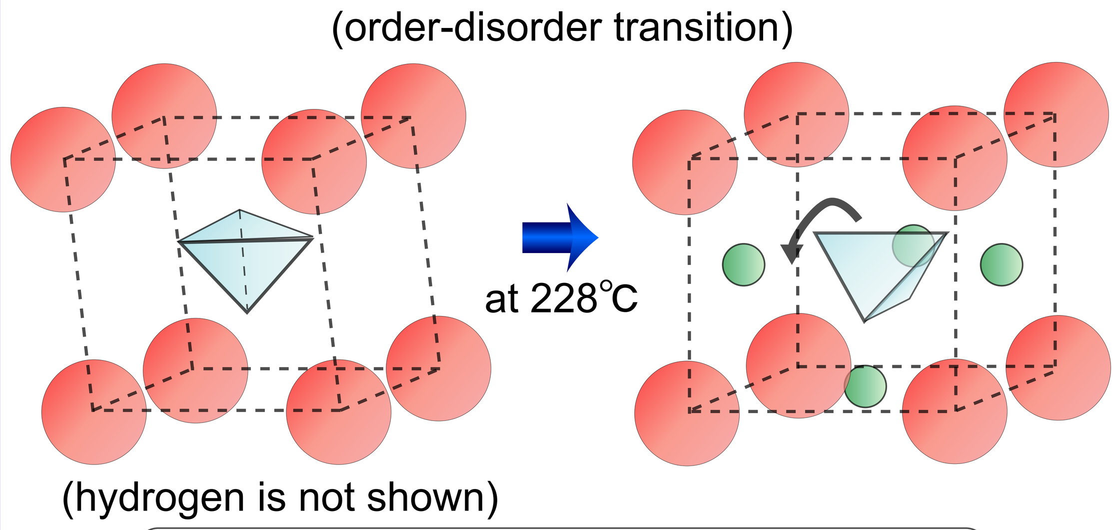
Introduction

Superprotonic conductor CsH_2PO_4

Superprotonic transition
(order-disorder transition)



CsH_2PO_4 (monoclinic) → CsH_2PO_4 (cubic) at 228°C
paraelectric phase — superprotonic phase
~10^{-6} [S/cm] — ~10^{-2} [S/cm]

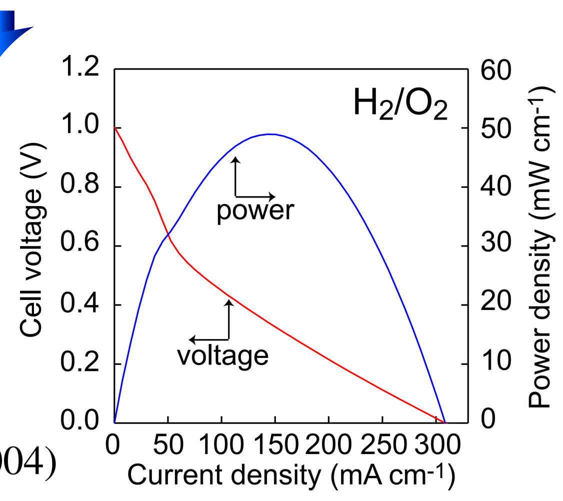
CsH_2PO_4 has a phase transition at 228 °C and exhibits a high proton conductivity around 10^{-2} S/cm.

New type fuel cell (solid acid fuel cell, SAFC)

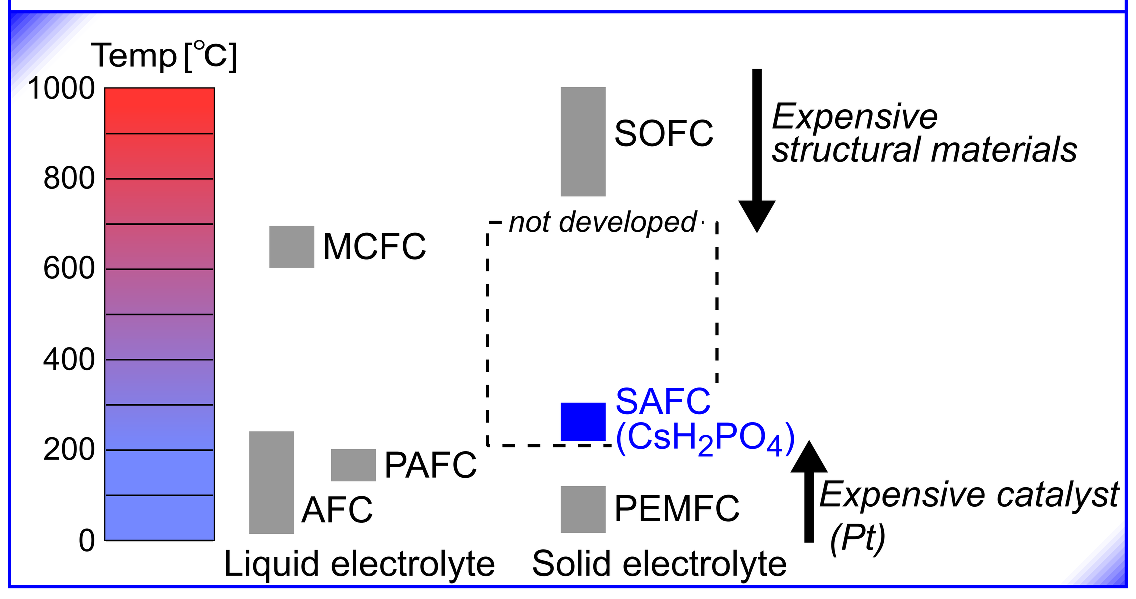
Thermodynamically stable under H_2 or O_2

CsH_2PO_4 is available as the electrolyte for an intermediate temperature fuel cell

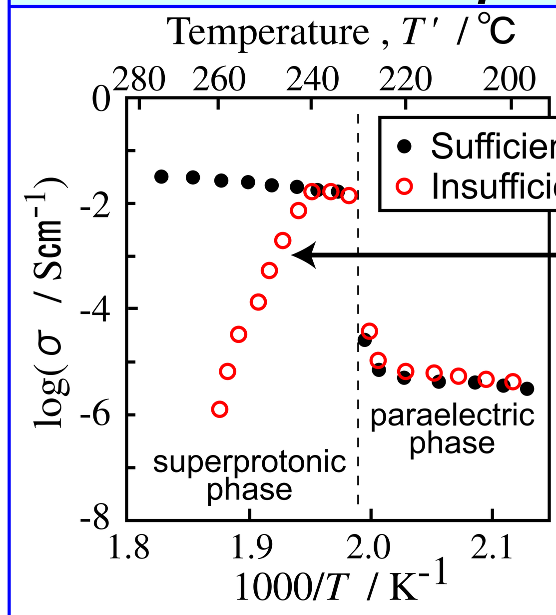
→ solid acid fuel cell (SAFC)



D.A.Boysen *et al.*, *Science* (2004)



Problem for the practical usage of SAFC



① What is the suitable humidified condition to suppress the dehydration of CsH_2PO_4?

② What is the dehydrated product? (there are two possibilities)

- $CsH_2PO_4 \rightarrow 1/2\ Cs_2H_2P_2O_7 + 1/2\ H_2O$ (pyrophosphate)
- $CsH_2PO_4 \rightarrow CsPO_3 + H_2O$ (metaphosphate)

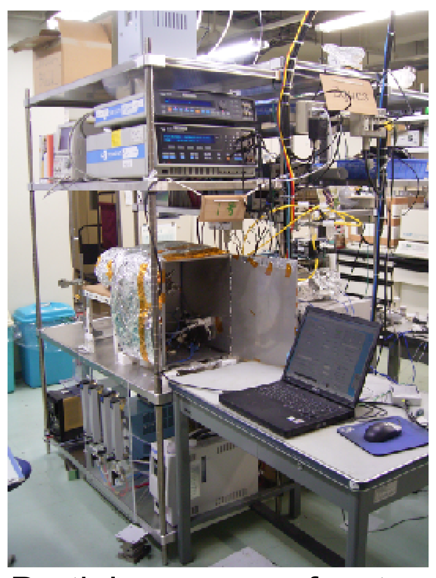
➡ Investigate the dehydration behavior of CsH_2PO_4 in the SAFC-operating temperature range of 230 to 260 °C

① Establish the relationship between the dehydration onset temperatures and water partial pressures
(conductivity measurement)

② Comprehensive estimation of the dehydration reaction
(thermogravimetry)
(equilibrium experiment)
(thermodynamic analysis)

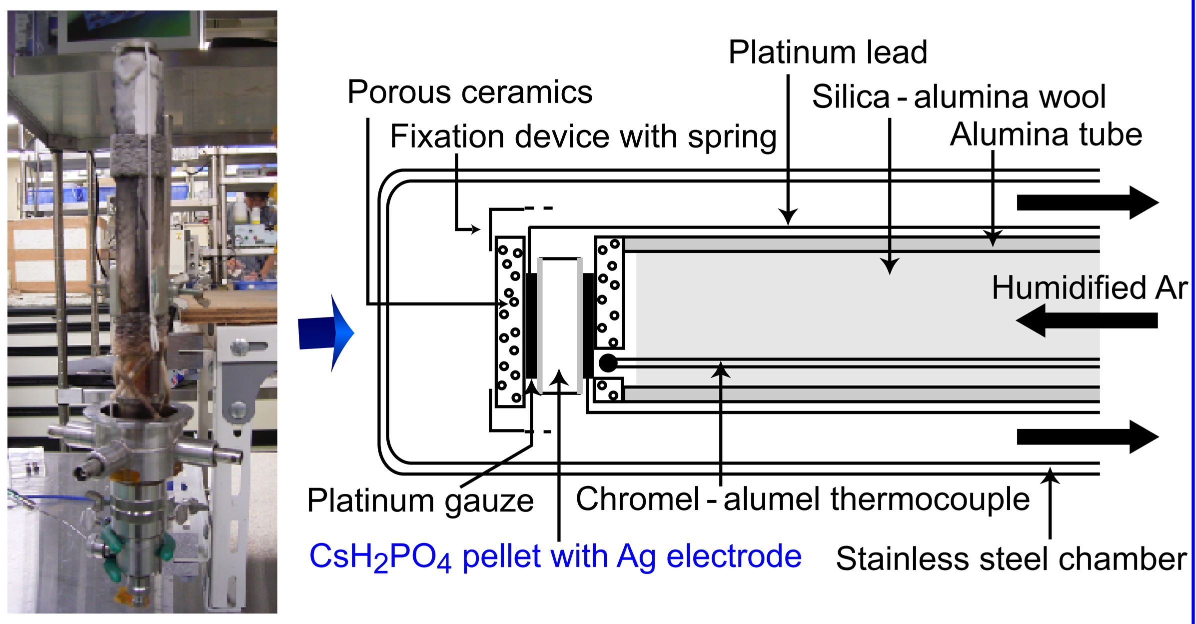
Experimental

Experimental apparatus



Partial pressure of water can be controlled at any aimed value from 0 to 1 atm

Sample holder for the conductivity measurement



Synthesize of CsH_2PO_4
Polycrystalline powder was synthesized from Cs_2CO_3-H_3PO_4 aqueous solution by the methanol- induced precipitation method

Conductivity measurement
Conductivity of the CsH_2PO_4 pellet was measured by an electrochemical impedance spectroscopy (EIS) using solartron 1260 impedance analyzer

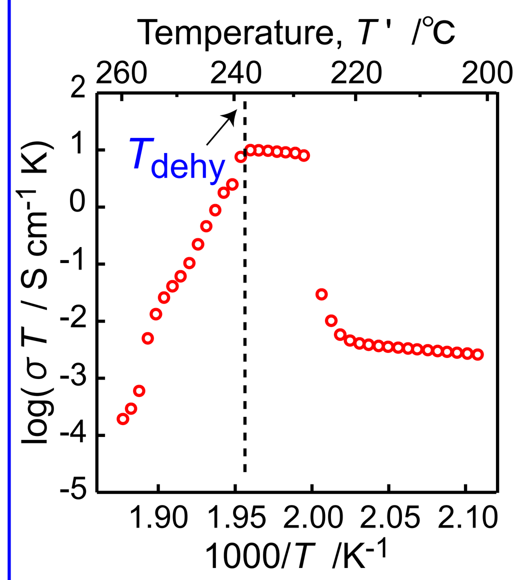
Thermogravimetry (TG)
TG under humidified condition was carried out using Rigaku TG-DTA/HUM

Equilibrium experiment
Equilibrium experiment was carried out at fixed temperature

Results & Discussion ①

Conductivity change

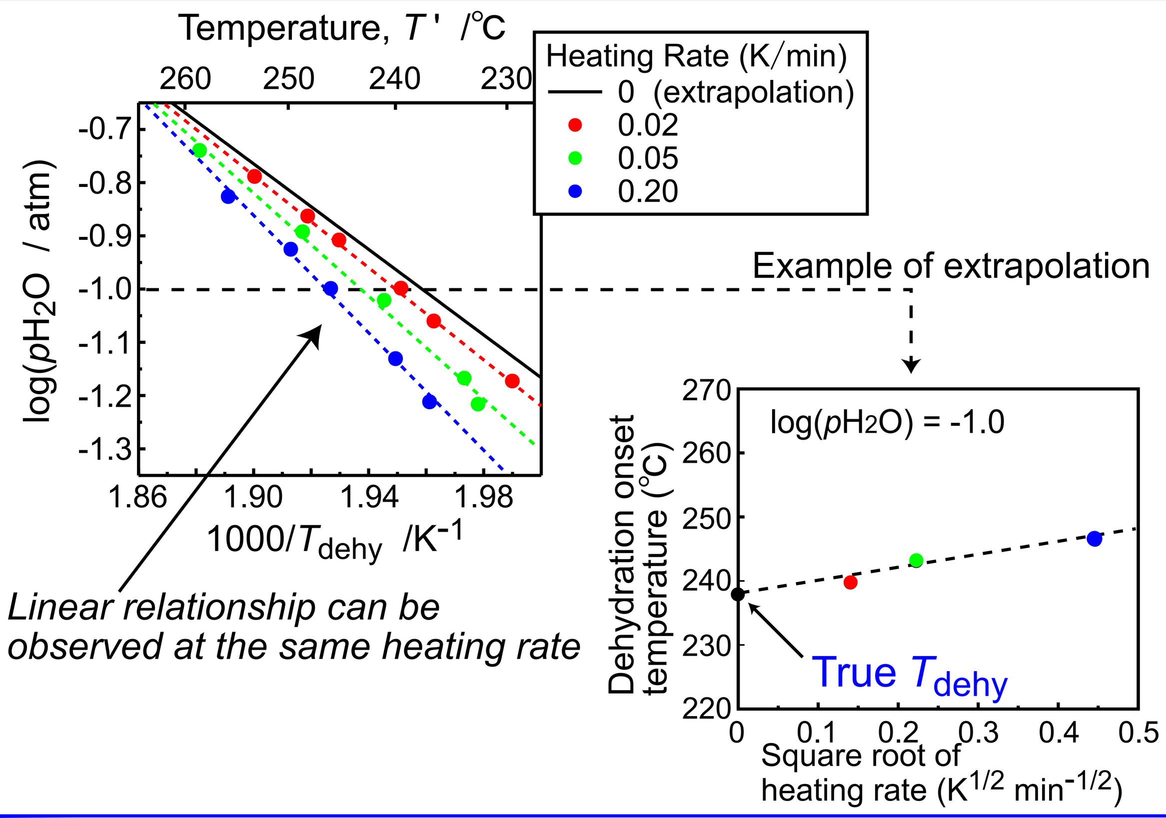
pH_2O = 0.087 atm
Heating Rate = 0.02 K/min



Temperature was increased at a constant heating rate

The temperature at which log(σT) starts to decrease is defined as the dehydration onset temperature (T_{dehy})

Dehydration onset temperature of CsH_2PO_4



Linear relationship can be observed at the same heating rate

T_{dehy} depends on the heating rate because the reaction rate of dehydration of CsH_2PO_4 is slow

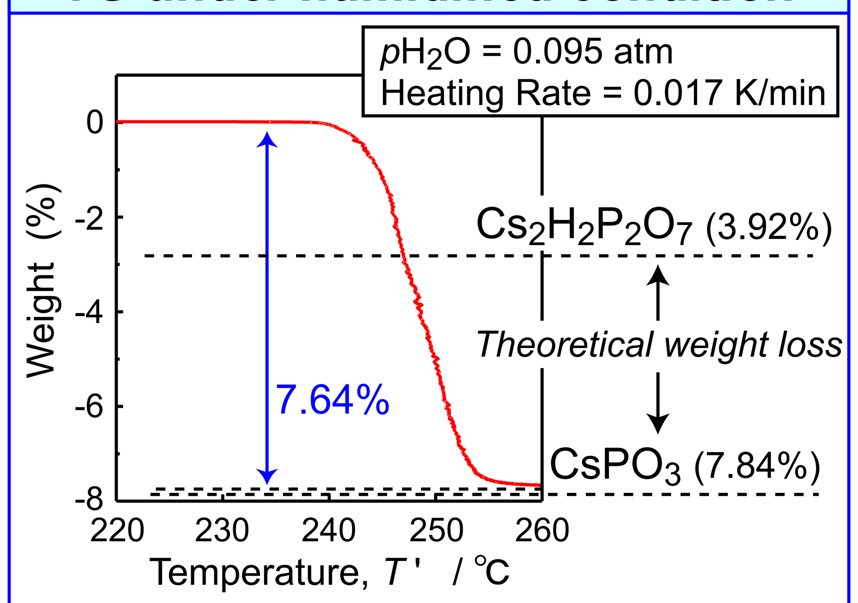
T_{dehy} should be extrapolated to a zero heating rate to determined the true values

$$\log(pH_2O\ /\mathrm{atm}) = 6.87(\pm 0.46) - 4.02(\pm 0.24) \times 1000\ /\ T_{dehy}$$
$230°C < T' < 260°C$

Results & Discussion ②

Observation of the dehydrated CsH_2PO_4 pellet
↓
Dehydration is solid/solid reaction

TG under humidified condition



Slope suggests no intermediate compounds in the course of dehydration to $CsPO_3$

Equilibrium experiment

pH_2O = 0.098 atm
Temperature 240°C
Time 48h

Just above the dehydration onset temperature + 3(±1.5) °C

Weight loss is 7.1 ± 0.5 %
↓
Product is not $Cs_2H_2P_2O_7$ (theoretical 3.92%)
↓
$CsH_2PO_4(s,sp) \rightarrow CsPO_3(s) + H_2O(g)$
sp : superprotonic phase

Thermodynamic analysis of the dehydrated product

ΔH, ΔS of dehydration

Thermodynamic equilibrium at T_{dehy}
$CsH_2PO_4(s,sp) = CsPO_3(s) + H_2O(g)$
↓
$\Delta G = 0$
↓
$$\log(pH_2O) = \frac{\Delta_{dehy} S^{\circ}(T)}{2.303 \cdot R} - \frac{\Delta_{dehy} H^{\circ}(T)}{2.303 \cdot R} \times 1000\ /\ T_{dehy}$$
↓
$\Delta_{dehy}H^{\circ}$, $\Delta_{dehy}S^{\circ}$ is almost constant in this narrow temperature range (230～260 °C)
↓
Comparing with the empirical relationship between the onset dehydration temperature and the water partial pressure
$\log(pH_2O\ /\mathrm{atm}) = 6.87(\pm 0.46) - 4.02(\pm 0.24) \times 1000/T_{dehy}$
↓
$\Delta_{dehy}H^{\circ} = 76.9(\pm 4.6)$ kJ/mol
$\Delta_{dehy}S^{\circ} = 132(\pm 9)$ J/mol K
$230°C < T' < 260°C$

$\Delta_f G$ of $CsPO_3$

Assume $\Delta_{dehy}H^{\circ}$, $\Delta_{dehy}S^{\circ}$ are constant from RT to 260°C
+
Consider the transition of CsH_2PO_4 at 228°C (superprotonic transition)
↓
Estimate $\Delta_f H^{\circ}$, $\Delta_f S^{\circ}$ of $CsPO_3$ at 298K
↓
Estimated values are compared with reported values

298 K		$\Delta_f H^{\circ}$ kJ/mol	$\Delta_f S^{\circ}$ J/mol K	$\Delta_f G^{\circ}$ kJ/mol
This study	$CsPO_3$(s)	-1235(±5)	-316(±10)	-1141(±10)
literature	$CsPO_3$(s)	-1241.4	–	–
	KPO_3(s)	–	-304.49	–

↓
Estimated values are reasonable
↓
The result of thermodynamic analysis reconfirms that the dehydrated product is $CsPO_3$
↓
$\Delta_f G^{\circ}(CsPO_3(s), 298K) = -1411(\pm 10)$ kJ/mol

Conclusion

We investigated the dehydration behavior of CsH_2PO_4 in the temperature range of 230 to 260 °C, which is the likely operational temperature window.

- The relationship between the onset temperature of dehydration and the partial pressure of water is expressed by the equation:

$$\log(pH_2O\ /\mathrm{atm}) = 6.87(\pm 0.46) - 4.02(\pm 0.24) \times 1000\ /\ T_{dehy}$$
$230°C < T' < 260°C$

- The dehydration reaction is as follows:

$CsH_2PO_4(s,sp) \rightarrow CsPO_3(s) + H_2O(g)$
sp : superprotonic phase

- The standard enthalpy and the standard entropy of the dehydration reaction in the temperature range of 230 to 260 °C are as follows:

$\Delta_{dehy}H^{\circ} = 76.9(\pm 4.6)$ kJ/mol
$\Delta_{dehy}S^{\circ} = 132(\pm 9)$ J/mol K
$230°C < T' < 260°C$

Furthermore, the standard Gibbs energy of formation of $CsPO_3$ at 298K was evaluated:

$\Delta_f G^{\circ}(CsPO_3(s), 298K) = -1411(\pm 10)$ kJ/mol