Chemical Heat Storage System with Redox Reaction for Medium-High Temperature Heat

Introduction

An enormous amount of **Medium-High Temperature Heat over 500 °C** is discharged into the atmosphere as **waste heat**.

e.g. 17,721 TJ/year from the steel industry in Japan[1)]

In order to establish a decarbonized society,

Promotion of utilization of medium-high-temperature heat over 500 °C is required.

◆ **Chemical Heat Storage system**
(Heat energy is stored and released by reaction heat.)

- O High heat storage density
- O Long-term heat storage in the form of chemical substances
- O No heat loss & No need of thermal insulation
- △ Complex system

Reaction system for CHS
- Hydration reaction
- Carbonation reaction
- **Redox reaction**

Heat storage (Reduction)

e.g. $6\ CoO + O_2 \rightleftarrows 2\ Co_3O_4$

Heat release (Oxidation)

Advantages of redox-type system:
- ✓ **High** heat storage density
- ✓ **Simple** reactor design
- ✓ **Oxygen** in the air = reactant & heat transfer fluid
- ✓ Gas tank is **not required,** atmosphere is **natural tank**

In this study:
- ✓ Cu-based spinel/delafossite couples with Mn and Fe as second cations were synthesized.
- ✓ Redox behavior of each sample, and cyclability of CuMn were investigated.
- ✓ Oxidation enthalpy of each reduced sample were measured.

1) 未利用熱エネルギー革新的活用技術研究組合 技術開発センター：産業分野の排熱実態調査 報告書(2019)

Experimental

～ Raw materials ～

Metallic nitrates: $Cu(NO_3)_2 \cdot 3H_2O$
$Mn(NO_3)_2 \cdot 6H_2O$
$Fe(NO_3)_2 \cdot 9H_2O$

Citric acid: $C_6H_8O_7$

Ethylene glycol: $C_2H_4(OH)_2$

Ammonia solution: $NH_3 \cdot H_2O$

～ Preparation ～

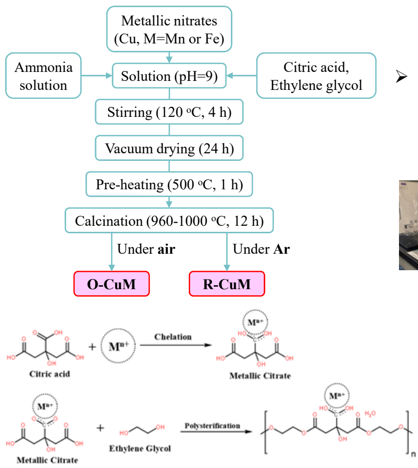

Fig. Preparation schematic

～ Characterization ～

- **Structure characterization**
  XRD (SmartLab, Rigaku)
- **Morphology**
  SEM (JSM-7500F, JEOL)
  For as-prepared and cycled samples
- **Redox behavior**
  TGA (STA7300, HITACHI)
  For as-prepared samples under air
- **Oxidation enthalpy**
  DSC (DSC-60, SHIMADZU)
  For reduced samples

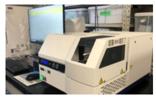

Fig. TGA apparatus

Fig. DSC apparatus

Fig. XRD apparatus

Results & Discussion

Characterization of CuMn & CuFe

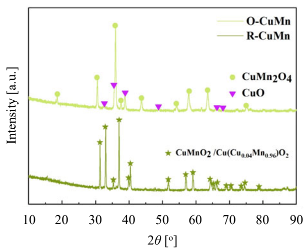

Fig. XRD pattern of CuMn

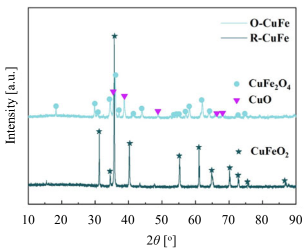

Fig. XRD pattern of CuFe

- ✓ O-CuM (M=Mn, Fe) showed a mixture of spinel (CuM_2O_4) and CuO.
- ✓ R-CuMn exhibited two similar phase, $CuMnO_2$ and $Cu(Cu_{0.04}Mn_{0.96})O_2$.
- ✓ R-CuFe showed pure delafossite ($CuFeO_2$) phase.

Oxidation Enthalpy of CuMn & CuFe

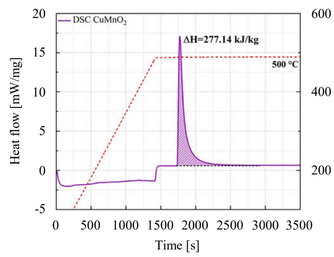

Fig. DSC curve of CuMn

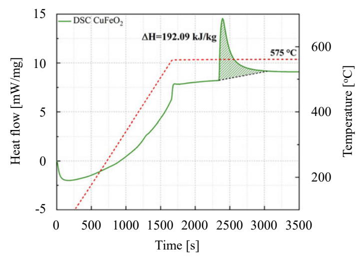

Fig. DSC curve of CuFe

Sample	Re-oxidation Temp. [°C]	Oxidation enthalpy [kJ/kg]	True Density [g/cm³]	Oxidation enthalpy [kJ/L]
R-CuMn	500	258.32±15.31	5.43	1402.68±83.13
R-CuFe	575	190.35±4.81	5.51	1048.83±26.50

Redox behavior of CuMn & CuFe

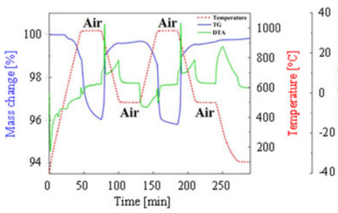

Fig. Redox behavior of CuMn

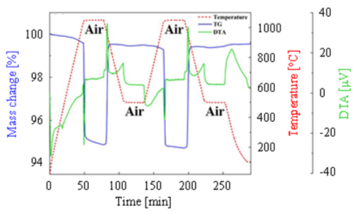

Fig. Redox behavior of CuFe

CuMn
- ✓ Reduction/Oxidation
  ⇒Approximately **4%** change in mass
- ✓ In the second cycle:
  Reduction started around **980 °C**
  Oxidation started around **900 °C**
  ⇒ Temperature hysteresis: 80 °C

CuFe
- ✓ Reduction/Oxidation
  ⇒Approximately **5%** change in mass
- ✓ In the second cycle:
  Reduction started around **1030 °C**
  Oxidation started around **950 °C**
  ⇒ Temperature hysteresis: 80 °C

Re-oxidation of R-CuMn in medium temperature region

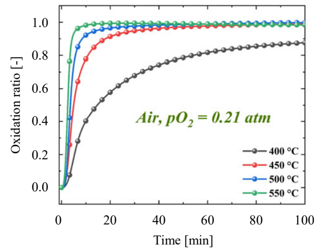

Fig. Oxidation ratio curve of R-CuMn

- ✓ Even at **450 °C**, oxidation finished within **30 min**.
- ✓ At lower temperature (**400 °C**), oxidation proceeded at **slower rate**.
- ✓ **R-CuMn** showed the ability to **oxidize in medium temperature region.**

Redox durability of CuMn

Durability test: Continuous heating and cooling steps from 500 to 1000 °C in air
Holding time of each cycle: 10 min

✓ CuMn is able to keep the **durability of redox reaction after 20 cycles.**

Conclusion

- ◆ Redox temperature of $CuMn_2O_4/CuMnO_2$ was in the range of 500-1000 °C, while $CuFe_2O_4$ requires higher temperature for reduction.
- ◆ $CuMnO_2$ achieved high oxidation enthalpy of 1.4 MJ/L-R-CuMn (258 kJ/kg-R-CuMn), while $CuFeO_2$ was 1.05 MJ/L-R-CuFe (190 kJ/kg-R-CuFe).
- ◆ $CuMnO_2$ showed the ability to oxidize in medium temperature region over 450 °C.
- ◆ CuMn is able to keep the durability of redox reaction after 20 cycles.

Contact

名古屋大学 大学院工学研究科 化学システム工学専攻 先進化学工学システム講座 化学エネルギーシステム工学
窪 田　光 宏（KUBOTA Mitsuhiro）
E-mail：kubota.mitsuhiro@material.nagoya-u.ac.jp