Cerium dioxide redox cycle for fuel production Thermodynamic modelling

B. Bulfin, F. Call, M. Lange, C. Sattler, R. Pitz-Paal, and I. V. Shvets





July 1, 2015

Contents

Introduction

- Motivation
- Solar Fuels and Thermochemical redox cycles

Model of the ceria redox system

- Development of model from equilibrium data
- Other ceria based oxides

Thermodynamics

- In-depth thermodynamic evaluation
- Efficiency maximisation and practicality of the cycle

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• We are interested in the thermochemical method of fuel production.

$$\begin{array}{ccc} \mathrm{MO}_{x} & \xrightarrow{\mathsf{Endothermic}} \mathrm{MO}_{x-\delta} + \frac{\delta}{2}\mathrm{O}_{2} & & \mathsf{Reduction} - T_{\mathrm{rd}} \\ \\ \mathrm{MO}_{x-\delta} + \delta\mathrm{H}_{2}\mathrm{O} & \xrightarrow{\mathsf{Exothermic}} \mathrm{MO}_{x} + \delta\mathrm{H}_{2} & & \mathsf{Oxidation} - T_{\mathrm{ox}} \end{array}$$

• MO_x is a metal oxide. $M = (Zn, Sn, Fe, Ce \dots etc.)$

Heat engine



- Efficiency of heat engine $\eta = \frac{W}{Q_{in}},$ with a maximum of $\eta_{Carnot} = 1 - \frac{T_C}{T_H}$.

Heat engine



- Efficiency of heat engine $\eta=\frac{W}{Q_{in}},$ with a maximum of $\eta_{Carnot}=1-\frac{T_C}{T_H}$.
- Efficiency of the thermochemical cycle is $\eta = \frac{\text{HHV}_{\text{H}_2}}{Q_{in}}$, with a maximum $\eta_{max} = \frac{\text{HHV}_{\text{H}_2}}{\Delta H_{\text{rd}}}$.
- $\rm HHV_{H_2}$ is the higher heating value of hydrogen Total energy available including latent heat of vaporisation of steam.

Cycle properties

- $\Delta G = \Delta H T \Delta S$. Reaction spontaneous for $\Delta G < 0$.
- Reduction + Oxidation = Water splitting: $\Delta G_{rd}(T) + \Delta G_{ox}(T) = \Delta G_{ws}(T)$

Cycle properties

- $\Delta G = \Delta H T \Delta S$. Reaction spontaneous for $\Delta G < 0$.
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• $\Delta H_{\rm rd} > \Delta H_{\rm ws}$ and $\Delta S_{\rm rd} > \Delta S_{\rm ws}$





• Ceria reduction: $\Delta H \approx 440 \text{ kJmol}^{-1}$ Water splitting: $\Delta H \approx 250 \text{ kJmol}^{-1}$ CO₂ splitting: $\Delta H \approx 280 \text{ kJmol}^{-1}$

• Ceria releases oxygen without any phase change (≈ 17 %). [Kümmerele 1999]

• Fuel production has already been demonstrated. [Chueh 2010]

• Ceria is relatively abundant (similar to copper).

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- Ceria is relatively abundant (similar to copper).

• Ceria can be partially reduced at high temperatures.

$$\operatorname{CeO}_2 \xrightarrow{heat} \operatorname{CeO}_{2-\delta} + \frac{\delta}{2}\operatorname{O}_2$$

• δ depends on P_{O_2} and T, $\delta(P_{O_2}, T)$.

Panlenar 1975

• No phase change implies a simple model.

$$\operatorname{CeO}_{2} \underbrace{\stackrel{\mathbf{k}_{\text{reduction}}}{\underset{\mathbf{k}_{\text{oxidation}}}{\overset{\mathbf{k}_{\text{reduction}}}{\overset{\mathbf{k}_{\text{reduction}}}}} \operatorname{CeO}_{2-\delta}^{+} \frac{\delta}{2} O_{2} \tag{1}$$

$$k_a = A_a \exp\left(\frac{-E_a}{RT}\right) \qquad \delta = \frac{[V_{\ddot{O}}]}{[Ce]}$$

Set a maximum value for δ, say δ_{max}.

Rate = Reduction – Oxidation

$$\frac{d\delta}{dt} = (\delta_{max} - \delta)A_{rd} \exp\left(\frac{-E_{rd}}{RT}\right) - \delta P_{O_2}^n A_{ox} \exp\left(\frac{-E_{ox}}{RT}\right)$$

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$$\begin{aligned} \mathsf{Rate} &= \mathsf{Reduction} \quad - \quad \mathsf{Oxidation} \\ \frac{d\delta}{dt} &= (\delta_{max} - \delta) A_{\mathrm{rd}} \exp\left(\frac{-E_{\mathrm{rd}}}{RT}\right) - \delta P_{O_2}^n A_{\mathrm{ox}} \exp\left(\frac{-E_{\mathrm{ox}}}{RT}\right) \end{aligned}$$



• At equilibrium
$$\frac{d\delta}{dt} = 0$$

$$\left(\frac{\delta}{\delta_{max} - \delta}\right) = \frac{A_{\rm rd}}{A_{\rm ox}} P_{O_2}^{-n} \exp\left(\frac{-\Delta E}{RT}\right) \qquad \Delta E = E_{\rm rd} - E_{\rm ox}$$

Rearrange to get

$$\log\left(\frac{\delta}{\delta_{max} - \delta}\right) = -n\log(P_{O_2}) + \log\left(\frac{A_{\rm rd}}{A_{\rm ox}}\exp\left(\frac{-\Delta E}{RT}\right)\right)$$

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Isothermal plots of equilibrium data.



• From the literature we have $\delta(P_{O_2},T)$

• The slope of each line is the parameter *n*.

[Panlenar 1975, Zinkevich 2006]

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Model vs. literature equilibrium

$$\left(\frac{\delta}{0.35 - \delta}\right) = 106000 \times P_{O_2}^{-0.22} \exp\left(\frac{-195.6 \,\left[\text{kJ mol}^{-1}\right]}{RT}\right)$$
(2)





- Isobaric plots of model
- Points are literature equilibrium data
- $\Delta E = 195.6 \pm 1.2 \text{ kJmol}^{-1}$ $\frac{A_{rd}}{A_{ox}} = 106000 \pm 10000 \text{ Pa}^n$ $\delta_{max} = 0.35$ $n = 0.22 \pm 0.013$

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Mixed oxides based on ceria



- Simple model which predicts $\delta(P_{O_2}, T)$, and naturally $P_{O_2}(\delta, T)$ also.
- Reduction + Oxidation = Water splitting: $\Delta G_{rd}(T) + \Delta G_{ox}(T) = \Delta G_{ws}(T)$
- $\Delta G_{\rm rd}(T) = -RT \ln(P_{\rm O_2}(\delta, T))$
- $\Delta G_{\rm ws}(T)$ is also known.
- The other thermodynamic properties for the reactions are known (C_p , ΔH ... etc).
- Have all the information for a full thermodynamic analysis.

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Heating efficiency

$$\begin{array}{ll} \operatorname{CeO}_{2-\delta_{\mathrm{ox}}} \xrightarrow{heat = \Delta H_{\mathrm{rd}}} \operatorname{CeO}_{2-\delta_{\mathrm{rd}}} + \frac{\delta_{\mathrm{rd}} - \delta_{\mathrm{ox}}}{2} \mathcal{O}_2 & T_{\mathrm{rd}} & P_{\mathcal{O}_2} \\ \operatorname{CeO}_{2-\delta_{\mathrm{rd}}} + (\delta_{\mathrm{rd}} - \delta_{\mathrm{ox}}) \mathcal{H}_2 \mathcal{O} \longrightarrow \operatorname{CeO}_{2-\delta_{\mathrm{ox}}} + (\delta_{\mathrm{rd}} - \delta_{\mathrm{ox}}) \mathcal{H}_2 & T_{\mathrm{ox}} & \mathcal{H}_2 \mathcal{O} \\ \Delta T = T_{\mathrm{rd}} - T_{\mathrm{ox}} & \Delta \delta_{\mathrm{eq}} = \delta_{\mathrm{rd}} - \delta_{\mathrm{ox}} \end{array}$$

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$$\eta_{max} = \frac{\text{HHV}_{\text{H}_2}}{\Delta H_{\text{rd}}}$$
. For ceria, $\eta_{max} \approx 67\%$.

• Additionally the temperature of ceria must be cycled.

$$Q_{\rm rd} = \int_{\delta_{\rm ox}}^{\delta_{\rm rd}} \Delta H_{\rm rd}(\delta) d\delta \qquad Q_{\rm CeO_2} = \int_{T_{\rm ox}}^{T_{\rm rd}} C_{p_{\rm CeO_2}}(T) dT \quad [\rm J\,mol^{-1}]$$
$$\eta_{\rm heat} = \frac{\Delta \delta_{\rm eq} \rm HHV_{\rm H_2}}{Q_{\rm rd} + Q_{\rm CeO_2}}, \tag{3}$$

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$$\Delta T = T_{\rm rd} - T_{\rm ox}$$
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$$m_{\rm rec} = \frac{\Delta \delta_{\rm eq} \rm HHV}{\rm H_2} \qquad (2)$$

$$\eta_{\text{heat}} = \frac{\Delta \delta_{\text{eq}} \Pi \Pi \Psi_{\text{H}_2}}{Q_{\text{rd}} + Q_{\text{CeO}_2}},\tag{3}$$

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• $T_{\rm rd}$ set to 1500 °C. Can increase $\Delta \delta_{\rm eq}$ by reducing $P_{\rm O_2}$.



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• Decreasing P_{O_2} comes with an energy cost.



$$\eta_{\rm fuel} = \frac{1}{Q_{\rm rd} + Q_{\rm CeO_2} + Q_{\rm N_2} + Q_{\rm gas} + Q_{\rm ox}}.$$

• Energy stored in fuel $\Delta \delta_{eq} HHV_{H_2}$. Yield by the higher heating value of the fuel.



$$\eta_{\rm fuel} = \frac{\eta_{\rm fuel}}{Q_{\rm rd} + Q_{\rm CeO_2} + Q_{\rm N_2} + Q_{\rm gas} + Q_{\rm ox}}.$$

• η_{plant} depends on solar concentration and reduction temperature T_{rd}



$$\eta_{\text{fuel}} = \frac{\eta_{\text{plant}} \Delta eq \Pi V_{\text{H}_2}}{Q_{\text{rd}} + Q_{\text{CeO}_2} + Q_{\text{N}_2} + Q_{\text{gas}} + Q_{\text{ox}}}$$

• Reduce Q_{rd} and heat ceria Q_{CeO_2} .



$$\eta_{\text{fuel}} = \frac{\eta_{\text{plant}} \Delta \delta_{\text{eq}} \text{HHV}_{\text{H}_2}}{Q_{\text{rd}} + Q_{\text{CeO}_2} + Q_{\text{N}_2} + Q_{\text{gas}} + Q_{\text{ox}}}.$$

• Produce $Q_{\rm N_2}$ and heat $Q_{\rm gas}$ the sweep gas.



$$\eta_{\rm fuel} = \frac{\eta_{\rm plant} \Delta \delta_{\rm eq} \rm HHV_{H_2}}{Q_{\rm rd} + Q_{\rm CeO_2} + Q_{N_2} + Q_{\rm gas} + Q_{\rm ox}}$$

• Heat the oxidiser $Q_{\rm ox}$

Ambient fuel production

$$\eta_{\rm fuel} = \frac{\eta_{\rm plant} \Delta \delta_{\rm eq} \rm HHV_{H_2}}{Q_{\rm rd} + Q_{\rm CeO_2} + Q_{N_2} + Q_{\rm gas} + Q_{\rm ox}}.$$
(4)

Fuel production efficiency with $\Delta T = 500$ °C.



• η_{fuel} can be maximised w.r.t. ΔT and P_{O_2} . Maximum is 4.5%.

• At maximum $\Delta \delta_{
m eq}$ is very small.

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Fuel production pumping



• Q_{gas} is now a small quantity of released heat.

Fuel production: pumping



• Q_{pmp} is the heat energy required to pump the oxygen.

Pumping efficiency

• The efficiency of vacuum pumps decreases with pressure.

Efficiency of some Bosch pumps



Current vacuum pumps not designed for efficiency.

• Pumping efficiency, $\eta_{pmp}(P) = 0.4 P^{0.543}$

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Reduced reduction pressure

$$\eta_{\text{fuel}} = \frac{\eta_{\text{plant}} \Delta \delta_{\text{eq}} \text{HHV}_{\text{H}_2}}{Q_{\text{rd}} + Q_{\text{CeO}_2} + Q_{\text{gas}} + Q_{\text{ox}} + Q_{\text{pmp}}}.$$
(5)

Efficiency with $\Delta T=$ 500 $\,^{\circ}\text{C}.$



• Dashed line $P = P_{O_2}$, which means $Q_{N_2} = Q_{gas} = 0$

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 Using the hot ceria from the reduction step to heat the relatively cool ceria from the oxidation step is a popular idea. [Miller 2008, Lapp 2013]



• Why bother? Instead use the heat as high temperature process heat for $Q_{\rm pmp}$ and $Q_{\rm ox}.$

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Ceria heat recuperation

- Assume the hot ceria can be used to decrease any of the other heat requirements with effectivness $\varepsilon_{\rm sld}=0.60.$



- Sharp peak occurs when $Q_{\rm pmp}+Q_{\rm ox}$ becomes larger than the available recycled process heat.
- Maximising efficiency w.r.t. ΔT and P gives $\eta_{\text{fuel}} \approx 11 \%$

$$\dot{n}_{\rm CeO_2} = \frac{\dot{Q}_{out}}{\Delta \delta_{\rm eq} \rm HHV_{H_2}} \; [\rm mol\,s^{-1}] \qquad \frac{\partial m_{\rm CeO_2}}{\partial \dot{Q}_{\rm out}} = t_{cyc} M(\rm CeO_2) \frac{\partial \dot{n}_{CeO_2}}{\partial \dot{Q}_{\rm out}} \; \; [\rm kg \; kW^{-1}]$$

Assuming $t_{\rm cyc} = 10$ min, $T_{\rm rd} = 1500~^{\circ}{\rm C}$ and $\varepsilon_{sld} = 0.6$

- Optimised ambient pressure, $\eta_{\rm fuel} \approx 7.5$ %, $\frac{\partial m_{\rm CeO_2}}{\partial \dot{Q}_{\rm out}} \approx 25 \ {\rm kg \ kW^{-1}}$. To power a Toyota Prius need 3750 kg
- Optimised pumped system, $\eta_{\rm fuel} \approx 11$ %, $\frac{\partial m_{\rm CeO_2}}{\partial \dot{Q}_{\rm out}} \approx 13 \ {\rm kg \ kW^{-1}}$.
- Very efficient pump $\eta_{pmp} = 0.5P^{0.27}$ (Transonic axial flow), $\eta_{fuel} \approx 18$ %, $\frac{\partial m_{CeO_2}}{\partial \dot{Q}_{out}} \approx 7 \text{ kg kW}^{-1}$.
- Solar electrolysis is 13 20 % efficient.

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- An analytical model of CeO₂ oxidation and reduction.
 <u>Brendan Bulfin</u>, Arran J. Lowe, Kevin A. Keogh, Barry E. Murphy, Olaf Lübben, Sergey A. Krasnikov, and Igor V. Shvets, *Journal of Physical Chemistry C* 46 (2013) 24129–24137
- Thermodynamics of CeO₂ thermochemical fuel production.
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