How can MIEC Membranes Facilitate Hydrogen Production from Water Thermolysis?

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April 29 2015

MIEC: Mixed Ionic-Electronic Conductive

Agenda

• 1. Hydrogen production
• 2. MIEC membrane reactors
• 3. Hydrogen production enhancement
• 4. Discussion
Hydrogen?

- Energy carrier!
- Expensive!

Hydrogen production is NOT cheap & NOT environment-friendly

- Cost [1]:
  - Water electrolysis: $4.14 – 5.12 /kg \text{H}_2$
  - Natural gas reforming: $1.7 /kg \text{H}_2$

- Goal set by DOE:
  - From renewables: <$2.00 /kg \text{H}_2$ [2]

- Production from hydrocarbons
  - ~ 9kg CO$_2$/kg \text{H}_2 [3]

* 1 kg \text{H}_2 ~ 1 gallon gasoline equivalent

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Water thermolysis can be an alternative energy storage approach

\[ x\text{CO} + \frac{3}{2}\text{H}_2 \rightarrow C_xH_y \]

- Water thermolysis
- Hydrocarbon partial oxidation

**LCF-91 membrane is an example**

- \( \text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta} \) is in perovskite structure
- Provided by Ceramatec

<table>
<thead>
<tr>
<th>Elements</th>
<th>La</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry</td>
<td>0.885 ± 0.023</td>
<td>0.115 ± 0.011</td>
<td>1.09 ± 0.025</td>
</tr>
</tbody>
</table>

**Lattice structure**

**Density of states**

- La/Ca
- Fe
- O
- O vacancy
At high T, some MIEC membrane surfaces love oxygen molecules.

Oxygen-containing molecules, such as H$_2$O, also react with oxygen vacancies.
**Experiment setup**

- **Feeding tube**
- **Humidifier**
- **Reactor**
- **MFC**
- **Shimazu GC2014**
- **Agilent 490 Micro GC**

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**Probes are used to measure local species concentrations**

- Measure inlet center (1) and outside of the feeding tube (2)

![Oxygen partial pressure profile](image)

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Narrower distance of the feeding tube on sweep side increases the oxygen flux

• But wider distance leads to less concentration polarization near membrane surface.

Water thermolysis

• Driving force: Heat and chemical potential difference

  • Schematic

\[
\begin{align*}
\text{H}_2\text{O} \rightarrow & \text{H}_2\text{O}^+ \rightarrow \text{H}_2 + 0.5 \text{O}_2
\end{align*}
\]
Homogeneous water thermolysis is a very slow process \cite{1,2}

\[ \begin{align*}
    \text{H}_2\text{O} + \text{M} & \rightleftharpoons \text{H} + \text{OH} + \text{M} \quad E = 440 \text{ kJ/mol} \\
    \text{H} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2 + \text{OH} \\
    \text{H} + \text{OH} & \rightleftharpoons \text{H}_2 + \text{O} \\
    \text{O} + \text{OH} & \rightleftharpoons \text{O}_2 + \text{H}
\end{align*} \]

- $990 \, ^\circ\text{C}$: the equilibrium $X_{\text{H}_2} = 1 - 16 \text{ ppm}$
- $t_{50} = 1100 \text{ s}$, $t_{50} = 512 \text{ s}$

Heterogeneous water thermolysis facilitates hydrogen production$^{[1]}$

- $t_{105} \sim 0.01 \text{ s}$
- $J_{\text{H}_2} \sim 0.002 – 0.01 \mu\text{mol/cm}^2\cdot\text{s}$ with inert sweep

\cite{2} Wu, X.Y., et al., PCCP, 2015, 17(15): 10093-10107
How to further facilitate water thermolysis reaction?

- 1. Increase potential difference
- 2. Decrease resistance: bulk diffusion and surface reaction

Higher temperature leads to more hydrogen production

- Oxygen diffusivity and surface reaction rates are both activated at higher temperatures
Fuel sweep can enhance the hydrogen production rate

- \( J_{H_2} \) reaches 0.1 \( \mu \text{mol/cm}^2\text{-s} \) with 5vol\% \( H_2 \) sweep
- \( J_{H_2} \approx 0.001 \mu \text{mol/cm}^2\text{-s} \) with inert sweep

Feed \( H_2 \) to sweep \( H_2 \) ratio is low

- Much hydrogen is used to split water

\[
\text{ratio} = \frac{\text{feed } H_2 [\text{scm}]}{\text{sweep } H_2 [\text{scm}]}
\]

- Other fuels?
Unfortunately, methane sweep has very hardly any improvements [1]

![Graph showing the comparison between reactive and inert sweep gases](image)

- Low reactivity
  - → increase surface areas for enhancement (porous layer)

Porous part is manufactured separately

- Dense + porous
  - Dense part is prepared by Ceramatec.
  - Porous part: Ceramatec LCF-91 powder + graphite

![Diagram showing the manufacturing process of porous and dense parts](image)
Porous surface enhancement layer on sweep side also facilitate hydrogen production rate

- $J_{H_2}$ reaches 0.15 $\mu$mol/cm$^2$-s with 5vol% CH$_4$ sweep
- $J_{H_2} \sim 0.001$ $\mu$mol/cm$^2$-s with inert sweep

Agglomeration or densification causes performance deterioration
Porous surface enhancement layer on feed side decreases the hydrogen production rate

- Inert sweep cases

![Graph showing the effect of temperature on hydrogen production rate.]  
![Graph showing the effect of temperature on hydrogen production rate.]

**Conclusion and further work**

- LCF-91 MIEC membrane can facilitate hydrogen production from water thermolysis

- Using fuel sweep and/or porous layer can further improve the hydrogen production rate

- Further analysis is needed to understand the heterogeneous reaction between H₂O and LCF-91
  - Relationship between surface area and enhancement
  - Surface active sites
  - Efficiency analysis with respect to oxygen permeation
Acknowledgement

- Sponsors:
  - Shell
  - KAUST

- Advisor: Professor Ahmed F. Ghoniem
- Lorraine
- Uddi, RGD labmates

Thanks!

Question?