SOLAR PRODUCTION OF HYDROGEN AND OXYGEN INCLUDING STORAGE THEREOF WITH SILICIDES IN WATER

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PATENT APPLICATION:
Generation of Hydrogen and Oxygen from Water and Storage thereof with Silicides 10 2005 040 255.0 (Germany) and PCT/EP application 2006 / 008333
THE CHALLENGE –
WE ARE APPROACHING A SOLUTION
Electrons are moved from the valence band to the energetically higher conduction band creating a "charge hole" in the valence band enabling the reduction and oxidation of water to yield hydrogen and oxygen, resp.

- An energetically appropriate bandgap is required for this purpose
- Furthermore, the sc should absorb light in the solar range of 300-800 nm
CONDUCTION-BAND, VALENCE-BAND AND BANDGAP ENERGIES OF SOME SEMICONDUCTORS

Potential (NHE), pH=7
An ideal semiconductor should have:

- Bandgap $> 1.23$ eV
- Conduction band $< -0.41$ eV
- Absorption of visible light $< 2.2$ eV
### POSSIBLE (SIDE) REACTIONS IN METAL-DRIVEN WATER SPLITTING

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Description</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$M + H_2O \rightarrow MO_n + H_2$</td>
<td>formation of hydrogen</td>
<td>energetically driven by metal oxide formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>forms oxide</td>
<td>(layer) thermally</td>
</tr>
<tr>
<td>2</td>
<td>$M + H_2O \rightarrow M + H_2 + \frac{1}{2} O_2$</td>
<td>water splitting</td>
<td>photochemically</td>
</tr>
<tr>
<td>3</td>
<td>$M + O_2 \rightarrow MO_n$</td>
<td>oxidation of catalyst by oxygen</td>
<td>thermally</td>
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</tbody>
</table>
Current investigations concern the mechanisms of ② and ③
HYDROGEN AND OXYGEN EVOLUTION KINETICS
(including partial hydrogen storage and very efficient oxygen storage)
PRESSURE DEPENDENCE OF WATER SPLITTING EFFICIENCY

$\eta = 4.5 - 11.5 \% \ (1.2 \text{ bar})$

(hydrogen evolution shown)
Hydrogen (sacrificial vs splitting) and oxygen production
UNLOADING OF OXYGEN FROM STORAGE

<table>
<thead>
<tr>
<th>Run</th>
<th>( \text{H}_2 ) (total in gas phase, ml)</th>
<th>( \text{O}_2 ) (ml) (^a)</th>
<th>( \text{H}_2 ) (sacrificial) (ml) (^b)</th>
<th>( \text{H}_2 ) (from water splitting, ml) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>&lt; 3 (^d,e)</td>
<td>&lt; 6</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>5 (^e)</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>12 (^e)</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>42</td>
<td>15 (^e)</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>103</td>
<td>43 (^e)</td>
<td>17</td>
<td>86</td>
</tr>
</tbody>
</table>

\(\text{H}_2\) (from water splitting, ml): Gas phase + 3 ml dissolved in water; \(\text{H}_2\) (total) - \(\text{H}_2\) (splitting); calc: ml \(\text{O}_2\) x 2; below detection limit in gas phase; unloaded by cooling-warming cycle. Exptl. error 5-10%.
(1) formation of passivating/catalytic/storage layer (thermal)
(2) water splitting ($\rightarrow$ $O_2 + 4H^+$) (light)
(3) reduction $2H^+ \rightarrow 2H^\bullet \rightarrow H_2$ (thermal)
(4) reversible storage of $H_2$ and $O_2$ (thermal)
ARE SILICIDE SEMICONDUCTORS IDEAL FOR WATER SPLITTING? - YES - INCLUDING REVERSIBLE STORAGE OF THE GASES

- Full solar light absorption (350 – 800 nm)
- Conduction band (CB) < H₂/H₂O (< - 0.41 eV)
- Valence band (VB) > O₂/H₂O (> + 0.82 eV)
- Cheap and abundant
- Reversible storage of hydrogen and oxygen under different reaction conditions (-> easy separation of the gases)
- Exothermic unloading of oxygen
- High efficiency of water splitting (presently ca 12%)
RESEARCH TEAM AND COOPERATIONS

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Dr. Andriy Kuklya
Klaus Kerpen
Marc-André Wüstkamp
Max Planck Institute for Bioinorganic Chemistry

Dr. Claudia Weidenthaler
Max Planck Institute for Coal Research

Prof. Dr. Horst Kisch
University of Erlangen

Dr. Jürgen Kleinwächter
BSR Solar Technologies, Lörrach
NEAR FUTURE GOAL: ONE-FAMILY HOUSE
HEATING TECHNOLOGY BY HPS
(Hydrogen Power System)

Demand: 12-15 kW h – 12-15 m³ H₂/day

Hydrogen Power System (present):
24 kg cat. / 60 m² / 0.6 m³ H₂/day (halogen light)
/ 3 – 12 m³ H₂/9 h (solar)
CATALYTIC COMPOSITION – TiSi$_x$ and/or oxides thereof?

$$\text{TiSi}_x \rightarrow \text{TiO}_2 : \text{Ti}(0) : \text{Si}_x(0) : \text{SiO}_2$$

Redox potentials

( - 0.41 eV to – 0.43 eV/ + 3.4 – 1.5 eV)
active form?

Generation of H$_2$
Generation of O$_2$
Light absorber

TiO$_2$ : Ti(0)
Si$_x$(0) : SiO$_2$
TiSi$_x$
Reactivity of TiSi$_x$

Current investigations concern the mechanisms of \( \text{O}_2 \) and \( \text{H}_2 \).
(1) formation of passivating/catalytic/storage layer (thermal)
(2) water splitting (→ O₂ + 4H⁺) (light)
(3) reduction 2H⁺ → 2H* → H₂ (thermal)
(4) reversible storage of H₂ and O₂ (thermal)
(1) formation of passivating/catalytic/storage layer (thermal)
(2) water splitting ($\rightarrow$ O$_2$ + 4H$^+$) (light)
(3) reduction 2H$^+$ $\rightarrow$ 2H$^\bullet$ $\rightarrow$ H$_2$ (thermal)
(4) reversible storage of H$_2$ and O$_2$ (thermal)
**Sources of Hydrogen**

- Hydrogen can be gained from reforming processes (e.g. catalytically from methane or propane)

  Disadvantages: *High pressure and temperature are required, besides methane and propane being fossil sources*

- **Biomimetics**: Attempts to mimic biosynthesis in green leaves in which nature produces primarily oxygen and protons (H\(^+\)), the latter of which could potentially be subjected to enzymatic transformation with a hydrogenase to form hydrogen.
A further and in our opinion in the near future technically realizable variant of „far-fetched biomimetics“ concerns the use of novel semiconductors (scs) as catalysts for „water splitting“ together with sunlight.

$$\text{Mn}_4 \text{ cluster} + [\text{NiFe}] \text{ cluster} \rightarrow \text{SC}$$
HYDROGEN AND OXYGEN EVOLUTION KINETICS

Phase A: Initiation
Phase B: Corrosion (major) and splitting (minor)
Phase C: Water splitting (exclusive)

The graph shows the kinetics of hydrogen and oxygen evolution over time. The phases are indicated as:

- Phase A: Initiation
- Phase B: Corrosion (major) and splitting (minor)
- Phase C: Water splitting (exclusive)

The data points are labeled with:
- a (H₂)
- b (H₂)
- c (H₂, reaction under air)
- a (O₂)

The graph includes points and lines indicating the evolution of hydrogen and oxygen over time, with specific measurements at various time intervals.
OUR OLD AND LITERATURE RESULTS

- Experiments with doped titanium dioxide (e.g. TiO$_2$ doped with ruthenium; 300-380-nm irradiation):
  - insufficient solar light absorption and catalysis
  - degradation of "catalyst"
  - applicable in water of high purity only

CURRENT RESEARCH ACTIVITIES

- Our hitherto most successful result in this area is based on the use of semiconductor-type nanomaterials which had so far not been used for water reduction and oxidation to produce hydrogen and oxygen, resp.:
  - Silicides: TiSi$_x$, V$_2$Si, ZrSi$_x$, Pt$_2$Si, MnSi$_2$ and Ni$_2$Si
  - 300-800-nm irradiation
How to improve ② vs. ③?

- reduce oxygen solubility in water layer
- doping of TiSi$_x$ with Pt or II / IV-valent MO$_x$
- control of metal impurities
- avoid Si and Ti contacts with water and oxygen by coating (Nafion membrane)
CONCLUSION

Superiority of the silicides:

• Not yet known literature-wise for the title application
• Cheap and abundant
• Thermal and light stability
• Adequate solar light absorption (350-800 nm)
• **BONUS: The silicides are able to store reversibly hydrogen at ambient temperature**

• Catalysis? 2:1 ratio for $\text{H}_2/\text{O}_2$ generation: $\rightarrow$ yes
• Modifications of the silicide compositions and surface engineering, as well as further technological improvements can likely secure the lead in this field.
SUMMARY OF CURRENT AND PLANNED R&D ACTIVITIES

- Further silicide nanostructures (FeSi_x, B_4Si, CoSi_2, MnSi_2, IrSi_2, Ti_3C_2Si, ZrSi_2, TaSi_2, CrSi_2 etc.)

- Surface engineering: a) Doping of the silicides, b) coating and c) in situ complexation of e.g. conducting HOR-type materials to the semiconductor surface

- Check light and sc concentration, temperature and pH dependence

- Evaluation of the reaction mechanisms, especially the fate of oxygen

- Immobilization of the silicides
Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit. Figure courtesy of P. Bonhôte/EPFL-LPI.


~20 nm particles
Scanning electron micrograph of the surface of a mesoporous anatase film prepared from a hydrothermally processed TiO₂ colloid. The exposed surface planes have mainly {101} orientation.

Wirkungsgrad ~10%
gute Langzeitstabilität
preiswertes Material
**Figure 1**
Principle of operation of photoelectrochemical cells based on n-type semiconductors. Cell that generates a chemical fuel, hydrogen, through the photo-cleavage of water.

**Figure 6** The Z-scheme of photocatalytic water decomposition by a tandem cell.

*M. Grätzel, Nature 414, 338 (2001)*
Photokatalyse mit neuen Halbleiternanomaterialien - Wasserspaltung

Titan-Silicid-Katalysatoren:

Vorteile: Nutzung des Bereichs des sichtbaren Lichts (350-800 nm)
Einsatz von normalem Wasser
hohe H₂-Erzeugungsraten
gute Langzeitstabilität
reversible O₂- und H₂-Speicherung bei RT

Zukunft: Fixierung auf /in polymeren (leitenden) Materialien
getrennte oder kombinierte O₂/H₂-Entwicklung
variables Ti:Si-Verhältnis

Demuth, Ritterskamp, Patentanmeldung 2005

Alte Experimente mit
1) TiO₂ dotiert
2) TiX (X ≠ O) / TM beschichtet

Nachweis der H₂/O₂-Entwicklung
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</tr>
<tr>
<td>3</td>
<td>$M + H_2O \rightarrow M+ H_2 + 1/2 O_2$</td>
<td>Water splitting</td>
<td>Photochemical</td>
</tr>
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**3 is not the case:**
- $H_2$: evolution due to metal oxide formation
- $O_2$: no evolution, consumption due oxidation

*Oxygen consumption is not dependent to hydrogen production*

**1 is not the case:**
- $H_2$: evolution due to water splitting
- $O_2$: evolution due to water splitting ($1/2$ to $H_2$) and consumption due oxidation

*As more hydrogen produced as less measurable consumption.*
measured hydrogen production and oxygen consumption

hydrogen production and calculated oxygen consumption at 50 and 20 degrees.
HYDROGEN PRODUCTION
WITH TiSi\textsubscript{2-4} FROM WATER USING HALOGEN LIGHT

![Graph showing hydrogen production over time.]

- 6-10 ml H\textsubscript{2} / day / g cat
- > 30 ml H\textsubscript{2} / day / g cat
(1) formation of passivating/catalytic/storage layer (thermal)
(2) water splitting ($\rightarrow O_2 + 4H^+$) (light)
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