Why don’t we have inexpensive PV systems made from Earth-Abundant elements?

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Harvard University

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San Francisco, CA
Photocatalytic Conversion of H_2O to H_2 and O_2
2 Strategies for Solar to Stored Energy

This symposium:

- $\text{H}_2\text{O} \rightarrow \text{H}_2$
- solar cell
- $\text{H}_2\text{O} \rightarrow \text{O}_2$

Our strategy:

- solar cell
- quinone $\rightarrow$ hydroquinone
- hydrogen bromide $\rightarrow$ bromine

- explosive $\text{H}_2$ gas
- electrocatalysts needed
- corrosion of solar cell

- non-flammable water solutions
- no electrocatalysts needed
- solar cell protected from water
The subject of my talk: My collaboration on a flow battery for grid-scale storage of electricity, the subject of Mike Aziz’s talk at 4pm today.

Quinone $\Rightarrow$ hydroquinone

Hydrogen bromide $\Rightarrow$ bromine

Solar cell
Outline

amount of solar energy

photovoltaic (PV) solar cells

abundant materials for large-scale thin-film PV

high-volume production of inexpensive thin-film PV

tin oxide – transparent electrode for PV
Solar Land Area Requirements - Global

Generating 15 TW (total primary power used by humans) with 15 % efficiency requires collector area

\[ = (15 \times 10^{12} \text{ W}) (200 \text{ W m}^{-2})^{-1} (0.15 \text{ efficiency})^{-1} = 5 \times 10^{11} \text{ m}^2 \]

Total land area of the earth is \( 1.5 \times 10^{14} \text{ m}^2 \)

Collector fraction = \( 5 \times 10^{11} \text{ m}^2 / 1.5 \times 10^{14} \text{ m}^2 = 0.0033 \)

0.33 % of land area could generate all the power now used
Solar Land Area Requirements - Global

20 TW from 6 Boxes at 3.3 TW Each
Solar Land Area Requirements - US

U.S. Land Area: $9.1 \times 10^{12}$ m$^2$

Average solar insolation: $>200$ W/m$^2$

U.S. Primary Power Consumption: 3.3 TW
U.S. Electricity Consumption = 0.4 TW

To supply all US primary power from PV:

$3.3 \times 10^{12} \text{ W}/(2 \times 10^2 \text{ W/m}^2 \times 15\% \text{ Efficiency}) = 1.1 \times 10^{11} \text{ m}^2$

Requires $1.1 \times 10^{11} \text{ m}^2 / 9.1 \times 10^{12} \text{ m}^2 = 1.2\%$ of Land Area

To supply all US electrical power from PV:

$0.4 \times 10^{12} \text{ W}/(2 \times 10^2 \text{ W/m}^2 \times 15\% \text{ Efficiency}) = 1.3 \times 10^{10} \text{ m}^2$

Requires $1.3 \times 10^{10} \text{ m}^2 / 9.1 \times 10^{12} \text{ m}^2 = 0.15\%$ of Land Area
Convenient truth: a small area can supply our electricity

At 10% efficiency, area needed for US electricity

PV on all US rooftops could meet US electricity demand
PV on my home in Cambridge, MA

20 panels of polycrystalline Si x 1.5 m$^2$/panel = 30 m$^2$

x 3 kWh / m$^2$ / day x 0.13 efficiency => 12 kWh/day

Average power 12 kWh/day x 1 day/24 h = 0.5kW

Typical household in US uses 1.3kW electric.

By replacing lights with LEDs and old appliances, we should be able to reduce our usage to 0.5 kW, the average input from our solar panels
Market Shares of PV Technologies

Mostly silicon, < 20 % thin films
Current Commercial PV Materials

Crystalline Si:
expensive purification, not integrated, (rare silver)

CdTe:
rare tellurium, toxic cadmium and tellurium

Amorphous Si-Ge:
low efficiency, slow deposition

Cu(In,Ga)Se₂ (CIGS):
rare indium, gallium, toxic selenium

Dye-sensitized:
rare ruthenium and platinum

None of these cell designs meet the criteria:
abundant, inexpensive and non-toxic elements
Why is PV Expensive?

Production is too slow

=> make solar cells very quickly

Too many separate pieces connected by wires

=> integrate directly without wires

Rare, expensive elements now used: Ag, In, Ga, Te, Se

=> use abundant and inexpensive elements: copper, zinc, tin, oxygen, sulfur, aluminum
How to make lots of inexpensive solar cells

- small amounts of materials
- high absorption coefficients => thin films

- rapid, continuous production on large areas
- < few seconds for depositing thin films

- integrated series interconnections of cells

- inexpensive, abundant elements

- nontoxic elements

- product durable for long lifetimes (> 20 years)
### Structure of CdTe Thin-Film Solar Cells

<table>
<thead>
<tr>
<th>Layer</th>
<th>Description</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>0.2-0.5 µm</td>
</tr>
<tr>
<td>CdS</td>
<td></td>
<td>600-2000 Å</td>
</tr>
<tr>
<td>CdTe</td>
<td></td>
<td>2-8 µm</td>
</tr>
<tr>
<td>ZnTe:Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-Paste with Cu, or Metals</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[Diagram showing the layers and thickness of the CdTe thin-film solar cell structure]
Band Diagram for a Thin-Film CdTe Solar Cell

- CdTe Absorber layer
- CdS hole-blocking layer
- ZnTe (Cu) Ohmic contact
- ZnTe electron-blocking layer
- Transparent conductor SnO$_2$(F)
- p$^+$, e$^-$, b
- h$^+$, h$^+$/b
- n$^+$
- i
How Much Material is Needed for Solar Cells?

A typical thin-film cell is $2 \, \mu m = 2 \times 10^{-6} \, m$ thick

The area required to supply current energy use is $5 \times 10^{11} \, m^2$

The volume of thin-film material is
\[ = (2 \times 10^{-6} \, m) \times (5 \times 10^{11} \, m^2) = 1 \times 10^6 \, m^3 \]

$10^6 \, m^3$ of Cu(In,Ga)Se$_2$ $\iff$ $1.4 \times 10^9 \, kg$ of indium
Total recoverable reserves of In in Earth’s crust $\sim 6 \times 10^6 \, kg$. enough to make 0.5% of the required solar cells

$10^6 \, m^3$ of CdTe $\iff$ $3.3 \times 10^9 \, kg$ of tellurium
Total recoverable reserves of Te in Earth’s crust $\sim 3.7 \times 10^7 \, kg$. enough to make $\sim 1 \%$ of the required solar cells
Which Elements are Sufficiently Abundant?

Enough Si, Al, Zn, Cu & Sn to make all the solar cells needed

Enough non-metals C, N, P, O, S, F, Cl, Br, I are available

Transition metals Fe, Mn, etc. don’t make efficient solar cells

Organics are unlikely to be stable for 20 years in sunlight

Avoid toxic elements like As, Cd, Se, Te, Be, Pb
### Thin-Film PV Absorbers Made of Abundant Elements

<table>
<thead>
<tr>
<th>Main Absorber Material</th>
<th>Band gap (eV)</th>
<th>Actual Efficiency</th>
<th>Theoretical Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS</td>
<td>1.1</td>
<td>5%</td>
<td>32%</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>2.0</td>
<td>5%</td>
<td>23%</td>
</tr>
<tr>
<td>Zn$_3$P$_2$</td>
<td>1.3</td>
<td>6%</td>
<td>33%</td>
</tr>
<tr>
<td>Cu$_2$ZnSn(S,Se)$_2$</td>
<td>1.3</td>
<td>13%</td>
<td>33%</td>
</tr>
<tr>
<td>(CH$_3$NH$_3$)Pb(I,Cl)$_3$</td>
<td>1.5</td>
<td>16%</td>
<td>33%</td>
</tr>
<tr>
<td>(CH$_3$NH$_3$)Sn(I,Br)$_3$</td>
<td>1.5</td>
<td>6%</td>
<td>33%</td>
</tr>
</tbody>
</table>

Zn$_3$P$_2$ + H$_2$O $\rightarrow$ PH$_3$ (highly toxic phosphine gas)

Selenium (Se) and lead (Pb) are toxic

(CH$_3$NH$_3$)Sn(I,Br)$_3$ is air-sensitive and water-soluble

More research is needed to improve their efficiency.
## Possible Scalable Materials for Solar Cells

<table>
<thead>
<tr>
<th>function of layer</th>
<th>possible materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>transparent support, protection</td>
<td>soda-lime glass</td>
</tr>
<tr>
<td>n+ transparent conductor, front electrode</td>
<td>SnO$_2$(F) or ZnO(F)</td>
</tr>
<tr>
<td>electron transparent, hole-blocking</td>
<td>Zn(O,S) or (Zn,Mg)O</td>
</tr>
<tr>
<td>light absorber, charge separator</td>
<td>SnS or Cu$_2$O</td>
</tr>
<tr>
<td>hole-transparent, electron-blocking</td>
<td>(Mo,W)O$_{3-x}$</td>
</tr>
<tr>
<td>reflective conductor, back electrode</td>
<td>Cu or Al</td>
</tr>
</tbody>
</table>

All elements sufficiently abundant, inexpensive & non-toxic
An Absorber with Abundant, Non-toxic Elements

Tin monosulfide, SnS

\[ \alpha > 10^5 \text{ cm}^{-1} \] strong absorption of visible light

→ need < 0.5 \( \mu \text{m} \) thickness to absorb 98% of light
Deposition of SnS Absorber Layer

Chemical vapor deposition or atomic layer deposition:

\[
\text{Sn} \quad \text{N_2} \quad \text{N} \quad \text{Sn} \quad \text{N} \quad \text{N} \quad \text{Sn} \\
\text{H}_3\text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{H}_3\text{C}
\]

or

\[
\text{Sn} \quad \text{N_2} \quad \text{N} \quad \text{Sn} \quad \text{N} \quad \text{N} \quad \text{Sn} \\
\text{iPr} \quad \text{iPr} \quad \text{iPr} \quad \text{iPr} \quad \text{iPr} \quad \text{iPr} \quad \text{iPr}
\]

\[+ \quad \text{H}_2\text{S}\]

Sang Bok Kim, Prasert Sinsermsuksakul, Adam S. Hock, Robert D. Pike, Roy G. Gordon

*Chemistry of Materials* **26**, 3065 (2014)
Current Champion SnS PV Cells

NREL-certified efficiency 4.36%
Best recent cell: 4.68%
Theoretical maximum: 32%

Sublimation of SnS Absorber Layer

SnS evaporates congruently like CdTe

=> 4% efficient solar cells

Could be produced rapidly by close-spaced sublimation as in First Solar’s CdTe process

Depositing Cu$_2$O
By Chemical Vapor Deposition or Atomic Layer Deposition:

H$_3$C
\[\text{CH}_3\]
\[\text{CH} \quad \text{H}_3\text{C}\]
\[\text{N} \quad \text{Cu} \quad \text{N}\]
\[\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3\]
\[\text{N} \quad \text{Cu} \quad \text{N}\]
\[\text{H}_3\text{C} \quad \text{CH} \quad \text{CH}_3\]
\[\text{CH}_3\quad \text{H}_3\text{C}\]

+ H$_2$O vapor

Hoon Kim, Harish B. Bhandari, Sheng Xu, Roy G. Gordon, 

By Electrodeposition from water-based electrolyte:

Yun Seog Lee, Danny Chua, Riley E. Brandt, Sin Cheng Siah, Jian V. Li,
Jonathan P. Mailoa, Sang Woon Lee, Roy G. Gordon, and Tonio Buonassisi,
*Advanced Materials* (2014); 10.1002/adma.201401054
Cu$_2$O Solar Cells

Methods for Improving SnS & Cu$_2$O PV Cells

More efficient collection by optimizing depositing and annealing:
- atmosphere with well-controlled activities of elements
- optimized time-temperature profile
- adding dopants to passivate grain boundaries

Improve back contact:
- higher reflectivity to near infrared light
- lower recombination velocity by reflecting electrons

Buffer layer
- wider band gap, so more transparent to blue end of spectrum
- reduced recombination rate near the junction
- higher conductivity buffer near the transparent conductor

Front contact:
- transparent conductor with lower work function
- more transparent front conductor
- antireflection coating
How windows are coated as the glass is made

SiO$_2$, Na$_2$CO$_3$ etc. in $\rightarrow$ glass out

The float process for making flat glass

Chemical Vapor Deposition (CVD) on glass just after it is made
CVD SnO$_2$ on hot glass ribbon

A given area of glass spends a few seconds under the coater.
CVD coaters in a glass factory

Makes very inexpensive tin oxide coatings (< $1 / m²)
The solar cells also need to be connected in series to increase the output voltage. To do this on-line, lasers should etch one layer selectively without disturbing the layers below. This avoids the high cost of wired connections between cells.
Why will On-line Solar Cells be Inexpensive?

Coater technology already developed for window coatings

Production costs: mainly precursor materials

Little energy input beyond what is used in glass production

Low handling costs because integrated into glass production

Low assembly costs because of integrated cell structure
Scientific and Technical Challenges

Find sufficiently rapid CVD reactions to make materials with:

- only abundant elements
- inexpensive precursors
- high purity
- few defects
- high speed deposition
- compatible ranges of deposition temperature
- stable and strongly adherent interfaces
CdTe thin film cells are currently the lowest cost PV.

First Solar Co. makes CdTe PV panels at <$0.60/peak watt.

The average energy production rate would be about 5 times lower, taking into account night and cloud cover.

Balance of system and installation would ~ triple the cost.

Thus, $0.60 \times 5 \times 3 \sim $9/average watt produced.

If the lifetime of the modules is 20 years, the cost of power is

\[
\frac{9}{[(8766 \text{ hrs/yr}) \times (20 \text{ yrs}) \times (1 \text{ kW} / 1000 \text{ W})]} \sim \$0.05 / \text{kW-hr},
\]

less than electricity from fossil fuel plus environmental costs.
“Look up, you fools!”
Summary

Solar energy can supply all human needs for energy

Inexpensive solar electricity can come from PV using solar cells made from earth-abundant elements

Production of the PV cells should be very fast integrated interconnections produced continuously during glass production

Storing electricity must be less expensive metal-free flow batteries (Aziz talk: 4pm today)
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- Paul Cizek (NREL) for certification of solar cells

- Precursors: Dow Chemical, Sigma-Aldrich and Strem Chemical

- U.S. National Science Foundation; U.S Department of Energy

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How Much Solar Energy?

1.2x10^5 terawatts of solar energy reaches earth’s surface

1 terawatt = 10^{12} watt = 10^{12} joules / second = 1 trillion watts
= 10^3 gigawatts = 10^6 megawatts = 10 billion 100 watt lights

One year contains about 8766 hours.

1.2x10^5 terawatt / 8766 ~14 terawatt ~ total human energy use

Energy in 1 hr of sunlight = total human energy use in a year