Alterations of glass surfaces and functional coatings for energy conversion systems

Joachim Deubener, Gundula Helsch
Alterations of glass surfaces and functional coatings for energy conversion systems

Functional Glasses: Properties and Applications for Energy & Information
January 7, 2013 Siracusa, Sicily, Italy

Outline

- Systems
  - National / EU energy conversion
  - Glasses
  - Coatings

- Alterations
  - Production
  - Storage
  - Service

- Tests
  - Performance
  - Warranty
  - Life cycle
“Mindful also of its responsibility toward future generations, the state shall **protect the natural foundations of life** and animals by legislation and, in accordance with law and justice, by executive and judicial action, all within the framework of the constitutional order.”

**German Basic Law, Article 20a**

*since 2002*
Germany mission

Renewable Energy Sources Act (EEG) since 2000 by the German Federal Ministry for the Environment

subsidies by feed-in tariffs (FIT):
every kWh that is generated from renewable energy facilities receives a fixed feed-in tariff (c/kWh) for 20 years.
hydro 7.7
wind 6.2-9.0
biomass 8.7-10.2
solar 50.6
degression 1-1.5 % / a

Electricity supply within a sustainable energy scenario for Germany. After 2030, renewable electricity will increasingly be employed for the generation of hydrogen for the transportation sector.

50 % renewable energy share in 2050
**Renewable Energy Sources Act (EEG)**

**short facts**

- 20.3 % of electricity, 11.0 % of heat and 5.5 % of fuel is generated from renewable energy (RE) sources in 2011, reducing Germany’s energy imports.

- Cut of 0.13 billion metric tons of CO$_2$ emissions only during 2010.

- Renewable energy industry employs (2011) 350,000 people in Germany.

- Germany hosts several world market leaders in RE technology and Germany is today among the world’s three major renewable energy economies.

- EEG serves as an archetype of similar legislation in other countries.

**sources:**
Federal Ministry BMU
German Energy Agency DENA
Renewable Energy Network 21, 2011
Renewable energy sources and their share of the energy supply in Germany

1) Sources: Targets of the German Government, Renewable Energy Sources Act (EEG); Renewable Energy Sources Heat Act (EEMageG), EU Directive 2009/28/EC;
2) Total consumption of engine fuels, excluding fuel in air traffic; 3) Calculated using efficiency method; source: Working Group on Energy Balances e.V. (AGEB), RES: Renewable Energy Sources; Source: BMU-KI III 1 according to Working Group on Renewable Energy-Statistics (AGEEE-Stat); image: BMU / Brigitte Hiss; as at: July 2012, all figures provisional.
renewable energy share 2010-2011
energy mix

electricity:
wind energy
> biomass
> PV
> hydro

heat:
biomass
> geothermal
> solarthermal
transformation of the energy system
“Energiewende”
recent issues

**nuclear power phase-out**
May 2011

after Fukushima nuclear disaster, Germany has permanently shut down 8 of its reactors and pledged to close: 1 in 2015, 1 in 2017, 1 in 2019, 3 in 2021 and the rest (3) by 2022.

Status of nuclear power globally

**nuclear power proponents**
- Operating reactors, building new reactor
- Operating reactors, planning new build
- No reactors, building new reactors
- No reactors, new in planning

**undetermined**
- Operating reactors, stable
- No reactors

**nuclear power oponents**
- Operating reactors, decided on phase-out
- Civil nuclear power is illegal

**sources:**
Ichabod Paleogene, Krzysztof Kori
Creative Commons
transformation of the energy system
“Energiewende”

recent issues

nuclear power phase-out
May 2011

after Fukushima nuclear disaster, Germany has permanently shut down 8 of its reactors and pledged to close: 1 in 2015, 1 in 2017, 1 in 2019, 3 in 2021 and the rest (3) by 2022.

PV-amendment
April 2012

after PV prize crash (towards grid parity), Germany reduced FIT for new installed facilities by ca. 40-45 %
from 28.7 (2011) to 17.0 (2013) c/kWh (< 10kW)
from 21.6 (2011) to 11.8  (2013) c/kWh (> 1 MW)

sources:
B. Burger „Energiekonzept 2050“ June 2010, FVEE,
Updated by Fraunhofer ISE Photovoltaik Report, Dec. 12th, 2012
PV industry crisis 2011-2012

- worldwide overproduction.
- Germany had a production capacity of 3 GW/a. China alone has a production capacity of 30 GW/a.
- dramatic fall in production costs.
- solar panels are becoming a commodity, and their production migrates to low cost countries, emerging countries for the most part.
- China offered huge credit lines with very low interest rates.
- market shakeout.
- most German producers went out of market (40,000 – 100,000 employees).

sources:
E. Weber (ISE), ParisTech Review, April 13th, 2012
### Transformation of the Energy System

#### “Energiewende”

#### Recent Issues

<table>
<thead>
<tr>
<th>Event</th>
<th>Date</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>Third Act Revision (EEG)</td>
<td>August 2012</td>
<td>After Arab Spring, Germany aims to speed up the expansion of offshore wind farms and north-bond fast grid system.</td>
</tr>
</tbody>
</table>
Global RE sources for meeting the 10TW renewable energy challenge in 2050

Renewable Energy Sources
- hydroelectric resource 0.5 TW
- from all tides & ocean currents 2 TW
- geothermal integrated over all the land area 12 TW
- globally extractable wind power 2-4 TW
- solar energy striking the earth 120,000 TW !!!

total solar irradiance 1.366 kW/m²

CSP potential electricity generation (GWh km² a⁻¹)

Land area theoretically required by CSP to supply the total expected world electricity demand in the year 2030 according to the IEA World Energy Outlook

concentrated solar power (CSP) in the EU-MENA potential 1700 TW

MENA = Middle East North Africa
DESERTEC Concept
CSP in EU-MENA

• founded in 2009

• harvesting sustainable power (CSP) from MENA desert regions.

• Using energy in EU via low-loss high-voltage direct current transmission (10–15% transmission losses between the desert regions and Europe).

Obstacles

• Central plants and transmission lines target for terror attacks.

• lack of long-term political stability in MENA region (Arab Spring since 2010).
The United Nations:
2 billion people across the globe live without electricity.
Off-grid electricity using cheap solar panels and high-efficiency LED lights is the most realistic option for many areas.
provide access to clean water
off-grid solar applications

The United Nations:
1.1 billion people live without access to clean water. That’s about one in six people in the world.

Desalination

Solar Stills
Glasses in energy applications

- fossil Power (?)
  - heat exchangers (enamels)
  - seals & flow distributors (glass-ceramics)

- hydropower (?)

- wind energy
  - glass fibre composites

- biomass (?)
  - cover glasses, tubes, concentrators, mirror substrates

- solar thermal
  - cover glasses, tubes, substrates, superstrates

- PV
  - cover glasses, substrates, superstrates

lack of glass applications in several key sectors!
coal power plant
rotary air-gas and gas-gas heat exchangers

air-gas exchangers
heating up air for combustion

gas-gas exchangers
heating up flue gas after DeSO\textsubscript{x} and before DeNO\textsubscript{x}

thick film coating: enamel
exchanger area $\approx$ 5-20 soccer fields
Glassy thick films for fossil power applications

Elements for gas-gas heaters have enamel coatings of:

- no open porosity,
- high acid resistance,
- edge coverage,
- small thickness tolerance to permit high element packing pressure, and
- complex profiles to induce turbulence.
Segmented panels for silos up to 7000 m³
to treat:
biogas digesters
sludge

have enamel coatings of:

- no open porosity,
- high acid resistance (inside)
- high resistance to atmospheric and UV corrosion (outside)
- easy cleanability
Glasses for solar bio-fuel generation

principles

biochemistry of solar powered $H_2$ generation

transparent glass reactors, vessels, and pipes

University Leiden, Solar fuels
The Netherlands, 2007
Chlamydomonas reinhardtii
(the green yeast)

- 1.6-2% PCE into H₂
- 5% medium term goal
- Fuel cell purity (>98%)
- 14 days
- Expected costs € 10/m²
- Prototyping stage 200-500 l

Provided by Uwe Kahmann

500 km pipeline
approx. 2000 m³
130 t algae p.a.

Klötzte (Wolfsburg)

http://www.ssnmr.leidenuniv.nl/content_docs/cleansolarfuels.pdf
Production issues:
- raw materials
- tank operation
- forming
- cooling
- storage

Glass performance:
- solar transmittance
- coatability
- robustness
- weatherability

Transmittance = 100 % – (Reflectance + Absorbance)

$R = \left( \frac{1-n}{1+n} \right)^2$

$\alpha = \varepsilon \times c \times d$

Solar glass = AR-coated + low iron + thin glass
Front glass

Status:
- d ≈ 3 mm
- floated, rolled (patterned)
- soda-lime-silica glass
- toughened (thermal)
- Fe < 100 ppmw
- AR-coated

R&D:
- improve failure resistance
  → thinner glass
- improve flat glass processing
  → integration of coating (TCO, AR, ion strengthening and alkali-barrier coatings) into production (in/on-line)
solar cover glasses
soda-lime-silica (PV, domestic water)

- 14 floated
- 6 rolled (slightly rippled)

soda-lime-silica glasses
72 - 15.5 – 12.1

composition by LA-ICP-MS
minor components and traces (iron conc.)

Total iron by LA-ICP-MS

Solar glass limit
Fe = 100 ppm (w/w)
iron speciation and redox
ferrous iron(II) by NIR-Photospectrometry

\[
\frac{[Fe^{2+}]}{[Fe_{total}]} \quad \text{using } \varepsilon = 53.8 \text{ l mol}^{-1} \text{ cm}^{-1} \\
\text{Ades (1990), Traverse (1992)}
\]
solar transmittance
EN 410

- integrating sphere
- $300 < \lambda > 2500$ nm
- normalized by AM 1.5

\[
\tau_e = \frac{\int_{0.3}^{2.5} T_{gh}(\lambda) \cdot S_\lambda \cdot d\lambda}{\int_{0.3}^{2.5} S_\lambda \cdot d\lambda}
\]

AM 1.5
solar transmittance vs. iron conc.

solar transmittance independent of floating/rolling process
Near surface chemistry (depth profiling) by Secondary Neutral Mass Spectrometry (SNMS) INA-X, Specs-Germany
solar glass surface chemistry (float)
as received

surface concentration by SNMS

sodium depletion air side > bath side

alterations due to different storage condition ($t$, $T$, $RH$, etc.)
crack initiation on sharp loading

Yoshida et al. 2004:

\[
\text{crack formation probability} = \frac{\text{# radial cracks}}{\text{# corners}}
\]

crack formation: bath > air

crack initiation load: air > bath
surfaces alteration (float glass)
storage conditions

- stack + separation powder
  - "open" = packing-free
  - "closed" = packed

- freshly produced
- 8 months open
- 2 months open + 6 months closed
- 1 month open + 7 months closed

alterations:
- air side > bath side
- closed > open
- pH uncontrolled > pH controlled
<table>
<thead>
<tr>
<th>Classification</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&quot;fresh&quot; surface</td>
</tr>
<tr>
<td>1</td>
<td>slight changes</td>
</tr>
<tr>
<td>2 + 3</td>
<td>crystals yard-free</td>
</tr>
<tr>
<td>4</td>
<td>crystals + diffusion yard</td>
</tr>
<tr>
<td>5</td>
<td>bumps dumps</td>
</tr>
<tr>
<td>6</td>
<td>dendrites</td>
</tr>
<tr>
<td>7</td>
<td>holes cracks, clouds</td>
</tr>
</tbody>
</table>

Irreversible alterations = non-washable

Type 4 crystals + diffusion yard

Classification of surficial alterations (storage) by E. Rädlein (TU Ilmenau)
AR coating market

Sol-gel improvements

- Solid silica particles
- Open porosity

- Core-shell particles (hollow sphere)
- Internal porosity

Competitive technologies

<table>
<thead>
<tr>
<th>Process limitations</th>
<th>Vacuum, multiple deposition</th>
<th>Acids, process control</th>
<th>High temperature cure</th>
</tr>
</thead>
</table>

AR coated cover glass for c-Si PV

- Sputtering
  - 4%
- Etching
  - 4%
- Sol-Gel
  - 92%

Production (mln. m²)

- 2012: Sol-Gel 92%
- 2015: Patterned 70%, Float 30%
- AR penetration cSi:
  - 2008: 0%
  - 2009: 5%
  - 2010: 10%
  - 2011: 15%
  - 2012: 20%
  - 2013: 25%
  - 2014: 30%
  - 2015: 35%

(DSM ARC (KhepriCoat))
<table>
<thead>
<tr>
<th><strong>Mechanical Durability</strong></th>
<th><strong>Environmental Durability</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Robustness</td>
<td>Coating Resistance to:</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Damp Heat</td>
</tr>
<tr>
<td>ASTM D3359</td>
<td>IEC 61215</td>
</tr>
<tr>
<td>Crosshatch Tape Test</td>
<td>UV Exposure</td>
</tr>
<tr>
<td>Abrasion Resistance</td>
<td>IEC 61215</td>
</tr>
<tr>
<td>EN 1096-2</td>
<td>Thermal Cycling</td>
</tr>
<tr>
<td>Felt Rub Test</td>
<td>IEC 61215</td>
</tr>
<tr>
<td>ISO 9211-3</td>
<td>Humidity Freeze</td>
</tr>
<tr>
<td>Blown Dust</td>
<td>IEC 61215</td>
</tr>
<tr>
<td></td>
<td>Acid Rain</td>
</tr>
<tr>
<td></td>
<td>EN 1096-2</td>
</tr>
<tr>
<td></td>
<td>Condensation</td>
</tr>
<tr>
<td></td>
<td>EN 1096-2</td>
</tr>
<tr>
<td></td>
<td>Salt Mist</td>
</tr>
<tr>
<td></td>
<td>ISO 9211-3</td>
</tr>
<tr>
<td></td>
<td>Outdoor exposure (IWI and rooftop)</td>
</tr>
</tbody>
</table>
Durability:

Long-term performance through unique closed pore nanostructure.

The advantage of the closed and smooth surface is the sharply reduced risk of hydrolysis – that means no water molecule penetration into the surface.

Proven durability in the laboratory and in-situ on life-sized modules:

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
<th>ΔT [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion resistance (EN 1096-2)</td>
<td>Felt rubbing</td>
<td>- 0,33 %</td>
</tr>
<tr>
<td>Immersion test</td>
<td>Immersion in 85°C water for 100 hours</td>
<td>+ 0,22 %</td>
</tr>
<tr>
<td>Immersion test saline</td>
<td>Immersion in 35°C salt solution (50 g NaCl per liter) for 100 hours</td>
<td>+ 0,05 %</td>
</tr>
<tr>
<td>Immersion test acid</td>
<td>Acid immersion in 35°C acid solution (0,1 M H₂SO₄) for 100 hours</td>
<td>+ 0,05 %</td>
</tr>
<tr>
<td>Vapor test</td>
<td>Exposure to water vapor</td>
<td>+ 0,21 %</td>
</tr>
<tr>
<td>Damp-heat test (IEC 61215)</td>
<td>Exposure to 85°C, 85% humidity for 1000 hours</td>
<td>+ 0,53 %</td>
</tr>
<tr>
<td>Thermal cycling test (IEC 61215)</td>
<td>200 cycles from -40°C to 85°C</td>
<td>- 0,12 %</td>
</tr>
<tr>
<td>Humidity-freeze test (IEC 61215)</td>
<td>10 cycles from 85°C, 85% humidity to -40°C</td>
<td>- 0,50 %</td>
</tr>
</tbody>
</table>

Our antireflective glass CENTROSOL HIT has undergone a number of qualification tests to determine its utility and resistance to ageing under realistic conditions.

1. Damp heat steady state test of AR glasses in conformity with IEC 61215
   Constant 85°C, 85% rh, 1,000 hours
2. Damp heat steady state test of AR PV modules acc. to IEC 61215
   Constant 85°C, 85% rh, 1,000 hours
3. Condensation water climate test of AR glasses acc. to DIN 50017 / EN 1096-2
   Constant 40°C, 100% rh, 480 hours
   Cycles: 40°C, 100 rh, 8 hours + 18-28°C, 75% rh, 16 hours, 5 ppm SO₂, 23 cycles
5. Thermal cycling testing of AR glasses in conformity with IEC 1215
   Cycles: -18°C/80°C, 56 cycles
6. Thermal cycling testing of AR PV modules acc. to IEC 1215
   Cycles: -40°C/+85°C, 200 cycles
7. Salt spray test of AR glasses acc. DIN 50021
8. Outdoor exposure tests at ISE Freiburg as part of IEA Task 27 (testing of different materials)
9. Outdoor exposure tests, exposure racks in Fürth, Forchheim, Freiburg
10. Salt fog impact testing of AR glasses acc. to IEC 1215
11. Frost test
    -20°C, 8 weeks, with ice formation
12. Boiling test
    10 min. boiling in deionized water at 100°C
13. Abrasion test acc. to EN 1096-2 (Crockmeter Test)
    Mechanical rubbing with felt fingers, weight 400 g, 1,000 cycles
heat-damp test

effect of “storage history“ on coating with single porous SiO$_2$ layer (sol-gel)

• Own measurements showed that float glasses with increased “storage history” had problems to withstand heat-damp test on the air-side but were intact on bath-side with crystals (washable).

196 h  85% RH, 85 °C

• Borosilicate glass tubes showed only slight changes with “storage history“ on heat-damp testing. AR-coat intact on both sides

196 h  85% RH, 85 °C

cootability depend on
degree of surface alteration (“storage history”)

à minimize storage
à seal fresh surface

... at least monitor quality
glass corrosion sensors

**Application:**
sensor plate at glass stack monitors environmental condition by colour changes and gives references for the coatability

**Innovation**
detection of glass corrosion by sensor plates
- glass segments with different corrosion sensibility
- pH-indicators of different transition ranges.

**Benefits**
- Recognizing of corrosive environmental influences to the glass during transport and storage.
- Sorting-out of damaged glass to assure quality previously.
- Economical advantages due to avoiding consequential losses and complaints.

source: patent application
DE 102009050714 A1
Alterations of nanoporous AR coatings due to aggregates of microorganisms and formation of biofilms

**adding of biocides**

→ Ag, Pd, Cu, .... (nano particles)

**adding of antimicrobial activity**

→ increasing hydrophobicity

→ photocatalytic oxidation (PCO)

*source: FORGLAS, Report 2012*
solar photocatalysis potentials

- photocatalytic oxidation (PCO)
- water purification: anti-bacterial
- air purification: volatile organic compounds (VOC), urban pollutants (NOx)
- solar fuel: hydrogen generation
- photoinduced hydrophilicity (PIH): easy-to-clean (Pilkington Glass (ActivTM), St-Gobain (BiocleanTM), PPG (SunCleanTM)), anti-fog

\[ h\nu > \Delta E_g \]

<table>
<thead>
<tr>
<th>oxide</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>0.93</td>
</tr>
<tr>
<td>CuO</td>
<td>1.7</td>
</tr>
<tr>
<td>CdO</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>3.9</td>
</tr>
</tbody>
</table>
**AR-coat with PCO**

anti-fouling


anatase stable despite curing > 500°C

outdore exposure started
AR-coat with PCO
HT-stability

sols of core-shell nano-particles

HT-stable anatase (1000°C) by interface passivation particle growth is retarded

Qi et al., in Handbook of functional Nanomaterials" (2013) in prep.

glasses for solar energy conversion systems
geometric concentration factor $C$

tower $\rightarrow$ $C > 1000$

trough $\rightarrow$ $C < 100$

PV, domestic water, photocatalytic $\rightarrow$ $C = 1$

Tg (°C) vs. CTE (ppm/K)

- silica
- alumo-borosilicate
- soda-lime-silica
- borosilicate

$T_g$ values and CTE for different glass types:
AR coatings for trough receiver tubes
borosilicate glasses

connected receiver tubes
each 4 m length
operating temperature ca. 400°C

source:
Flabeg,
Glas und Solar, Otti 2012
AR coating on borosilicate glass tubes

minimizing alterations due to mechanical impacts:
goal: highly adhesive long-term abrasion resistant ARC

was achieved inter alia by chemical modifications

Nanoporous silica-rich layer
\( n_{\text{eff}} = 1.33 \), porosity: 37 %, thickness: 110 nm

Transmittance (%)

Wavelength (nm)

Schott PTR\textsuperscript{TM}70

depth profiles (SNMS)

Krzyszak, M. et al. German pat., 2003, DE 10209949 A1
Chinese pat., 2007 CN CN 1319889C
Accelerated aging tests
projection of lifetime performance

Calculated acceleration factors vs. aging test temperature for different aging mechanisms, i.e. activation energies, (operating temperature 400°C)

170 kJ/mol

<table>
<thead>
<tr>
<th>Minimum aging time [h]</th>
<th>Aging temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>510</td>
</tr>
<tr>
<td>643</td>
<td>525</td>
</tr>
<tr>
<td>295</td>
<td>560</td>
</tr>
<tr>
<td>93</td>
<td>590</td>
</tr>
<tr>
<td>16</td>
<td>660</td>
</tr>
<tr>
<td>6</td>
<td>700</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
</tr>
</tbody>
</table>

Length of test necessary for 550 °C working temperature during 25 years:
- ~ 1000 days at 590 °C
- ~ 170 days at 660 °C (maximum test temperature)

Source: M. Arntzen in: Glas und Solar, Otti 2012
Thermal alterations of AR on silica glass windows for volume pressure receivers

Solar tower research facility
Plata Forma Solar Almeria, Spain

300 heliostates
12,000 m² reflecting surface
85 m

1 m² receiver window
Silica glass

Receiver 1000 °C hot air
Focused sunlight
AR coated transparent cover glass
ARTRANS 2007-2009 (DLR)

thermal calculations
4% efficiency gain

window design
(stacked tube segments)

coating
SiO₂ containing porous layer
(1.2 m x 1.2 m)

assembling and test run
(2010)

loss of energy in the receiver by

➢ convection
➢ radiation

1000 °C

Antireflective coating for compensation of reflective losses

silica glass window

➢ thermal insulation

3% reflected sunlight
Thermal alterations of AR coating on silica glass windows for volume pressure receivers


- solar transmittance as a quantitative measure of the densification process

- viscosity based mechanism of densification in agreement with 3D-shrinkage of porous SiO2 soots & powder compacts (Scherer 1976, Sacks & Tseng 1984)
Soltrac II – alliance (DLR, Heraeus, Abengoa, TUC)
2012-2014

Soltrec - high temperature pressurized volumetric air receiver

thermal alterations of AR coated and uncoated silica window (TUC)

“Arizona” dust

source: Roman Korzyńczuk, Reiner Bück, Ralf Uhlig

*Abengoa Solar NT, Rambla del Olímpico Olímpico 11, 1* planta, 04001 Almería, Spain
1. Deutsche Zentrum für Luft- und Raumfahrt e.V., Pfefferwaldring 38-40, 70569 Stuttgart

14. Kölner Sonnenkolloquium

Arizona dust 1200°C 30 min

25 mm