



NASF SURFACE TECHNOLOGY WHITE PAPERS  
82 (12), 1-38 (September 2018)

The 54<sup>rd</sup> William Blum Lecture  
Presented at NASF SUR/FIN 2018  
in Cleveland, Ohio  
June 4, 2018

## Innovative Applications of Electroplating and PVD for New Material Solutions

by  
Dr. Lars Pleth Nielsen

for

Dr. Per Møller

Recipient of the 2017 William Blum  
NASF Scientific Achievement Award





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**Editor's Note:** The following is the Powerpoint presentation for Dr. Møller's William Blum Memorial Lecture at SUR/FIN 2018, in Cleveland, Ohio on June 4, 2018. Due to Dr. Møller's serious illness, he was unable to make the journey to SUR/FIN. In his stead, his longtime professional colleague, Dr. Lars Pleth Nielsen, of the Danish Technological Institute (DTI), presented the lecture.

## William Blum Scientific Achievement Award

### Innovative applications of electroplating and PVD for new material solutions

*Prof. Per Møller,  
Technical University of Denmark (DTU)*

*and*

*Dr. Lars Pleth Nielsen,  
Danish Technological Institute (DTI)*



Slide 1 - Title.

## NASF SURFACE TECHNOLOGY WHITE PAPERS 82 (12), 1-38 (September 2018)

### Introductory material

There was great concern about the outlook for Dr. Møller's health, and Dr. Nielsen began the lecture by reporting on his current status (Slide 2). While the matter was very serious, the good news was that a stem cell donor had been found and the prognosis was good.

### William Blum Lecture



### Prof. Per Møller sends his regards

### Per is temporary grounded and unable to present his William Blum Lecture

- Diagnosed with MDS special sub-group of bone marrow cancer
  - Low red blood cells, low platelets and low white blood cells
- Treatment will include chemotherapy and stem cell transplantation.
- The good news – a donor with optimal match has been identified.
- Per is currently being prepared for stem cell transplantation.
- The overall prognosis is good.

Slide 2 - Dr. Møller's health status.

Dr. Nielsen also shared some of the published news items, both here and in Denmark, that covered the good news that Dr. Møller had received the Scientific Achievement Award for 2017 (Slides 3-4).

### William Blum Scientific Achievement Award

#### TEKNOLOGIPRIS

Professor **Per Møller**, Institut for Mekanisk Teknologi på DTU, har modtaget William Blum's Scientific Achievement

**Award.**  
Den prestigefyldte pris uddeltes af NASF, som er den amerikanske brancheorganisation for cve teknologien (National Association for Surface Finishing).

Prisen gives til en personlig og praktisk har brydende forskning og udvikling i området for elektrokemi og overflækkens

med åbningsceremonien på den amerikanske SURFIN-2017-konference i Atlanta, Georgia.

Det er kun ganske få forskere uden for USA, der har modtaget prisen, og professor Per Møller sætter med prisen dansk forskning og udvikling inden for avanceret overfladeteknologi på verdenskortet.

Som begrundelse for tildeling af prisen nævnes mange års virke har bidraget til internationalt og ikke mindst udgivelser i teknologiske

intertwined world of applied surface engineering'.

NASF udaler bl.a. om bogen, der blev

vet til i tæt samarbejde med Lars Pleth

Nielsen, Teknologisk Institut:

'Det er det

største og mest betydningsfulde værk

skrævet inden for overfladeteknologi de

sidste 40 år'.

Med den ærefulde pris følger bl.a. Willi-

am Blum Møller.

Per Møller siger:

'Mine forskningsinteresser omfatter

monion på

2018. Pol



## NASF SURFACE TECHNOLOGY WHITE PAPERS 82 (12), 1-38 (September 2018)

### William Blum Lecture



#### SCIENTIFIC ACHIEVEMENT AWARD DR. PER MØLLER, TECHNICAL UNIVERSITY OF DENMARK

The Scientific Achievement Award recognizes a person who has contributed to the advancement of the theory and practice of electroplating, metal finishing and the allied arts; raised the quality of processes and products; enhanced the dignity and status of the profession; or has been involved in a combination of these efforts. The first recipient of this award was Dr. William Blum, Sr., who was instrumental in the establishment of fundamental research in the Society.

This year, we were very pleased to recognize Dr. Per Møller for this prestigious award. His accomplishments in the technology of surface finishing and his contributions to our industry are both wide and in depth. Most notably, he has contributed the modern "bible" of our industry, the two-volume *Advances in Surface Technology*, as important to the engineer today as Blum and Hogaboam's *Principles of Electroplating and Electroforming* was in the 1930's.



- Highlighted:
  - Contributions to surface finishing
  - Contributions to industry are both wide and in depth
  - The two-volume Advanced Surface Technology known as the surface "bible"

I will do my very best to exemplify and underline these points

Slide 4 - Plaudits on the Award (2).

Dr. Nielsen was the perfect person to deliver the lecture in Dr. Møller's stead. The two are a very close team, and have collaborated on numerous research projects, and have published numerous papers and books together (Slide 5).

### William Blum Lecture

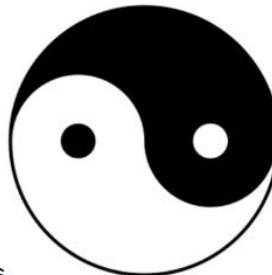


- I have known Per for more than 15 years
- We have worked extremely close together and initiated numerous projects
  - Commercial projects
  - R&D projects
- Written several books together
- Right now we are writing on a corrosion book
- We are going into energy: H<sub>2</sub>, CH<sub>4</sub> upgrading, biogas cleaning, CH<sub>3</sub>OH synthesis

"If you can't afford the "professor" you can always get the "doctor"....



Chemist  
Wet based coatings



Physicist  
Vacuum based coatings

Slide 5 - Long-time collaborators Møller and Nielsen.

## NASF SURFACE TECHNOLOGY WHITE PAPERS 82 (12), 1-38 (September 2018)

It was noted that Dr. Møller was dedicated to the surface finishing field, his mind constantly on the lookout for examples of metal finishing performance in the field. At SUR/FIN 2015 in Rosemont, Illinois, Dr. Nielsen pointed out that the many attractions in the Chicago area (Slide 6), were superseded by Dr. Møller's interest in examining the corrosion performance of street hardware in the city (Slide 7).

### Surfin 2015, Chicago

**Chicago Travel Guide**  
USA  
#3 in Best Shopping Destinations in the USA

Overview    Things to Do    Hotels    Dining    When to Visit    Getting Around    Neighborhoods    More \*

**Best Things To Do in Chicago**

Chicago has all the offerings you'd expect from a major city: world-class museums, vibrant shopping districts and ample nightife venues, just to name a few. If you're here to learn, plan to spend a fair amount of time in Grant Park: This area is home to such notable institutions as the Art Institute of Chicago and The Field Museum. For a more Windy City-centric education, start your vacation with an architecture river cruise – which can provide background on Chicago's famous skyscrapers like the Willis Tower and Tribune Tower – before exploring the city's innovative roots at the Museum of Science and Industry. Just save time for some of the city's quintessential experiences like catching a game at Wrigley Field and window-shopping along The Magnificent Mile. How we rank Things to Do.

All Things To Do    Free    1-Day Itinerary    2-Day Itinerary    3-Day Itinerary

**Art Institute of Chicago**  
#1 in Chicago  
Local Pick: Must-see



Stephens Convention Center, Rosemont, IL, USA  
Slide 6 - Tourist activities in Chicago.

### Surfin 2015, Chicago



Stephens Convention Center, Rosemont, IL, USA  
Slide 7 - Dr. Møller's activities in Chicago.





## NASF SURFACE TECHNOLOGY WHITE PAPERS 82 (12), 1-38 (September 2018)

Dr. Nielsen outlined the lecture (Slide 7), which was in essence a career retrospective of the work of this very talented man. He began the lecture by noting that "surfaces are everything," noting that surfaces, through control of their properties, are essential to everything in our world, from the scientific technologies to mundane everyday products (Slide 8). The emphasis of the talk related to current efforts in sustainable energy made possible by electrochemical technology.

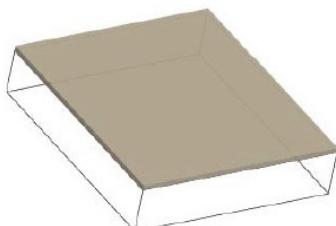
### William Blum Lecture



- Examples of Per Møller's patent portfolio
  - Some highlights
- Examples of books
  - Advanced Surface Technology
  - Our upcoming corrosion book
- Energy
  - Hydrogen - from lab to large-scale
  - Biogas - Upgrading CO<sub>2</sub> to CH<sub>4</sub>
  - Ideas on methanol
- Self-cleaning paints
- Antibacterial surfaces
- Summarizing

Slide 8 - Blum Lecture outline.

### Surfaces are everything



Wear resistance  
Tribological properties  
Magnetic properties  
Electrical conductivity  
Solderability/weldability  
Hardness  
High temperature resistance  
Corrosive resistance  
Biocompatibility  
Hydrophobic/hydrophilic properties  
Catalytic properties  
Self cleaning properties  
Friction properties  
Color and appearance  
Decorative appearance  
Refractive index  
Oxide formation/passivation

Slide 9 - Surfaces are everything.



# NASF SURFACE TECHNOLOGY WHITE PAPERS

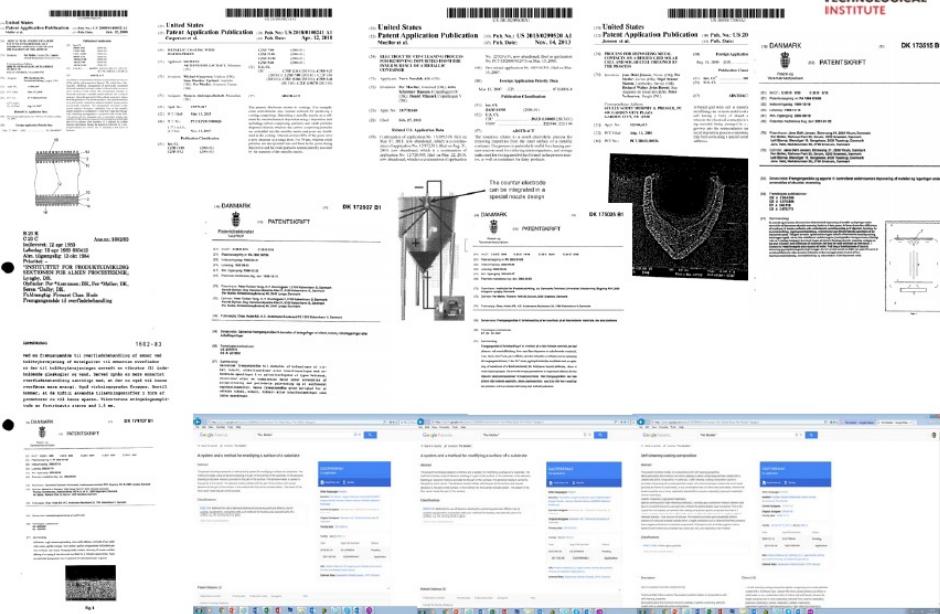
## 82 (12), 1-38 (September 2018)

## Patents

Dr. Møller has been awarded numerous patents (Slides 10-15). In the patent portfolio, is a method for manufacturing implantable medical devices (Slide 11; US Patent 5,772,864 (1998)), by electroforming a prosthesis on a dissolvable mandrel. Another involves a process for electrodepositing copper wire contacts on silicon-based solar cells (Slide 12; with BP Solar; US Patent 6,881,671 (2005); European patent appl.). Another patent cites a unique slip ring, using electrodeposited rhodium for wind turbines (Slides 13-14; Vestas Wind Systems; WO/2001/061795 (2001)). Dr. Møller was instrumental in the development of a process for producing stress-free nickel and cobalt electrodeposits (EP0835335B1) for Daimler Benz Aerospace. This was the key to the use of additive layer manufacturing (ALM) of the rocket engine for the Ariane Vulcan 2 (Slide 15).

Dr. Nielsen pointed out that years of experience with innovation have given Dr. Møller the ability to motivate students and collaboration partners to develop components and devices which create meaningful solutions instead of focusing on useless patents.

## Patents



Slide 10 - Selection of Møller patents.

**NASF SURFACE TECHNOLOGY WHITE PAPERS**  
**82 (12), 1-38 (September 2018)**



US005772864A

**United States Patent [19]**

Møller et al.

[11] Patent Number: **5,772,864**

[45] Date of Patent: **Jun. 30, 1998**

[54] METHOD FOR MANUFACTURING  
IMPLANTABLE MEDICAL DEVICES

5,328,587 7/1994 Fenske ..... 205/73  
5,352,512 10/1994 Hoffman ..... 428/311.51

[75] Inventors: Per Møller, Lyng; Jørgen  
Kamstrup-Larsen, Allerød, both of  
Denmark

1542939 3/1979 United Kingdom .

FOREIGN PATENT DOCUMENTS

iraxcenter Course of Coronary S

Ruygrok and Claudia Sprenger

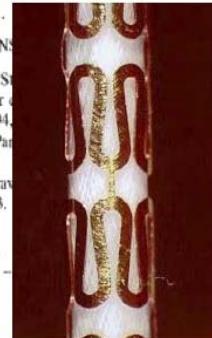
: Netherlands, Dec. 15-17, 1994-

me for Metal Micromechanical Pa

wenheim, Electroplating, McGraw-Hill, 1978, pp. 426-441, 160-163.

Examiner—Bruce F. Bell

Examiner—William T. Leader



Slide 11 - Electroformed stents.



Europäisches Patentamt

European Patent Office

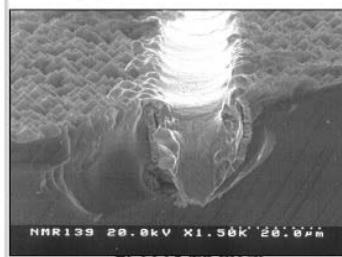
Office européen des brevets



(11) EP 1 182 709 A1

(12)

EUROPEAN PATENT APPLICATION



GB GR IE IT LI LU

(51) Int Cl.7: H01L 31/0224, H01L 31/068,

H01L 31/18

(71) Applicants:

- IPU, Institutet For Produktudvikling  
2800 Lyngby (DK)
- Enthon-OMI (Benelux) B.V.  
6999 BC 's-Hertogenbosch (NL)

Development of a process for depositing  
metal contacts on a buried grid solar cell  
and a solar cell obtained by the process.  
(2000) Patent application nr: EP  
00610081.2-1235

(72) Inventors:

- Jensen, Jens Dahl  
2830 Virum (DK)
- Møller, Per  
3200 Esbjerg (DK)
- Møller, Lars  
2100 Copenhagen (DK)
- Verner, Claus  
5200 Odense (DK)



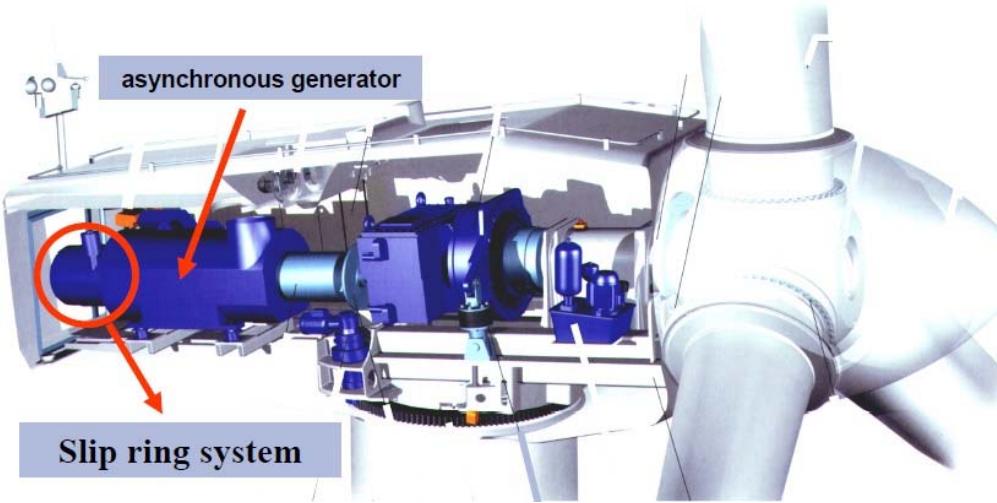
(74) Registered Office:  
Copenhagen  
1750 Copenhagen (DK)

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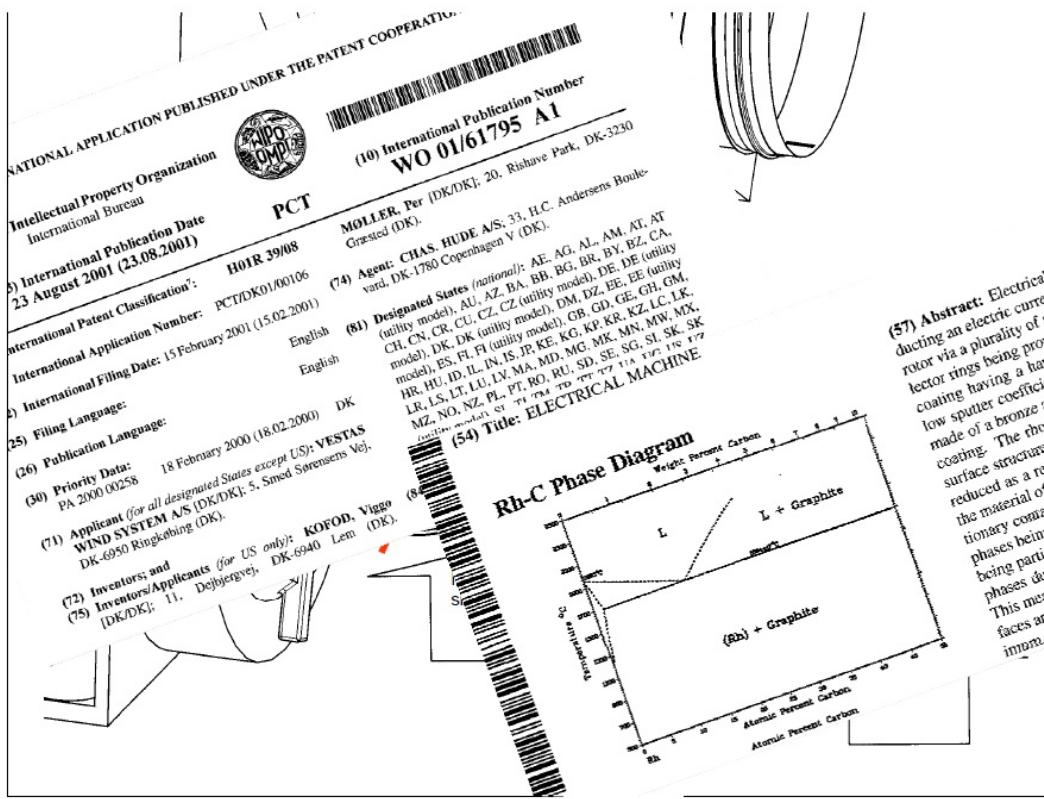
Slide 12 - Deposited metal contacts and solar cells.

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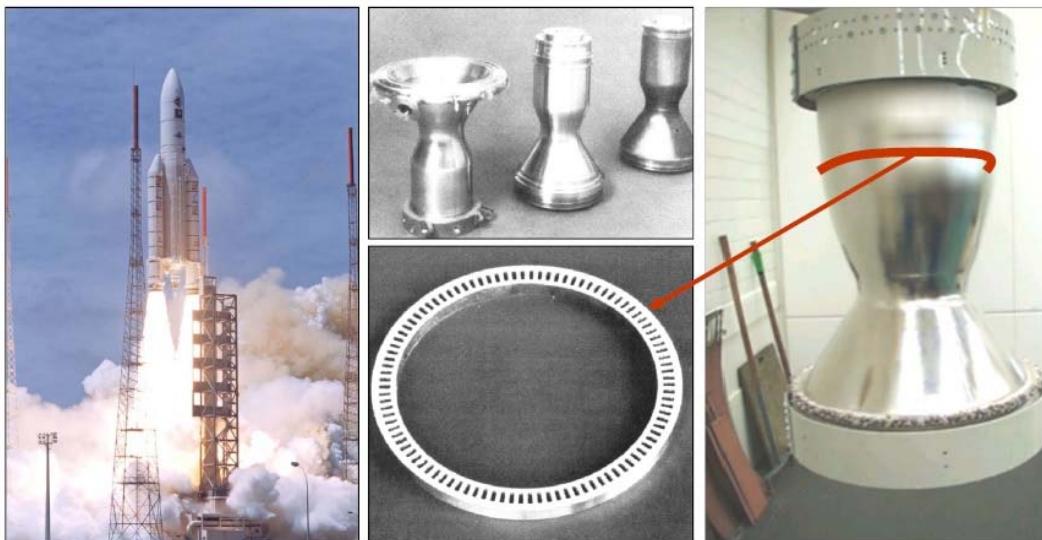
Slide 13 - Slip ring in wind turbine generator (1).



Slide 14 - Slip ring in wind turbine generator (2).

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## Patents; Space (Ariane)



### Electroplating production method, EP 0835335B1

Slide 15 - Additive layer manufacturing for a rocket engine.

## Published Books

### Examples of books



Slide 16

Dr. Møller has published many papers and a number of books during his career, but the most significant one was published in 2013. Co-authored with Dr. Nielsen, the two-volume, 1240-page *Advanced Surface Technology* was lauded as the most comprehensive text on surface engineering technology published to date (Slides 17-19). Currently in development is another text which promises to be as important as *Advanced Surface Technology* - a new book on corrosion, *Understanding Corrosion from an Applied Perspective* (Slide 20). In addition to the information shown in Slide 20, for the chapter on corrosion types, topics will include (a) introductory material; (b) thermodynamics and the equilibrium potential; (c) corrosion potential, polarization and Pourbaix diagrams and (d) optimal material and surface selection for corrosion protection.



## NASF SURFACE TECHNOLOGY WHITE PAPERS 82 (12), 1-38 (September 2018)

### Advanced Surface Technology



2 volumes – 1240 pages

It took us 4 years to write...

Slide 17 - Advanced Surface Technology (1); Covers.

### Advanced Surface Technology

*"It is truly a **surface bible**," VOM, association for surface finishing techniques, Belgium*



*"The present two-volume set of Advanced Surface Technology is arguably the **most comprehensive** ever to be published in the field of surface finishing. Drs. Per Møller and Lars Pleth Nielsen have devoted years of effort to provide, in their words, 'a holistic view on the extensive and intertwined world of applied surface engineering,'" NASF, National Association for Surface Finishing, USA.*

*"The books are clear and the schematic setting makes the reading very pleasant and interesting even for those who are simply looking for up-to-date information and data..... the English language is not an obstacle to understanding. It is clear and linear. This **book should not miss among the technical manuals** of those who are interested in surfaces and their property. It's definitely a good tool for those who work in technical offices or produce finishes or treatments on metals, as well as offices and, of course, included in the reference manuals, of whom teaches at the University or in Master Class dedicated to surfaces", Enzo Strazzi, Association for Aluminum Surface Treatment, Aital Oxit, Italy.*

Slide 18 - Advanced Surface Technology (2); Plaudits.

## NASF SURFACE TECHNOLOGY WHITE PAPERS

### 82 (12), 1-38 (September 2018)



## Advanced Surface Technology

- Wear and friction properties of surfaces
- Introduction to corrosion
- Basics of electrochemistry
- Introduction to chemical and electrochemical processes
- Guidelines for electrochemical deposits
- Electroplating of zinc
- Electroplating of nickel
- Electroplating of copper
- Electroplating of tin
- Electroplating of chromium
- Electroplating of precious metals
- Electroplating of alloys
- Electroless plating of metals
- Chemical and electrochemical polishing
- Conversion coatings
- Introduction to gas phase processes and plasma
- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD) Industrial PVD and CVD processes
- Ion-beam processes
- Thermochemistry and diffusion processes
- Hot-dip galvanizing
- Vitreous enamel
- Thermal spraying and hardfacing
- Mechanical plating
- Introduction to paint
- Classification of paints
- Special paints and special application methods
- Pre-treatment prior to painting
- Selection of paint systems
- Characterization of surfaces and materials
- Measuring hardness
- Measuring the "total visual appearance" of surfaces
- QC; Thickness and adhesion of coatings
- Corrosion evaluation and durability testing
- Thermodynamic consideration
- Pourbaix diagrams

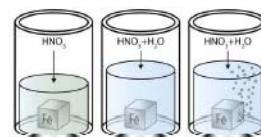
Slide 19 - Advanced Surface Technology (3); Contents.

## New Corrosion book

- 4. Corrosion types**
- 4.1 Introduction to corrosion types  
 4.2 Even or uniform corrosion  
 4.3 Galvanic corrosion  
     4.3.1 Factors influencing galvanic corrosion  
 4.4 Selective corrosion  
 4.5 Localized corrosion  
     4.5.1 Crevice corrosion  
     4.5.2 Pitting corrosion  
     4.5.3 Filiform corrosion  
 4.6 Cover corrosion  
 4.7 Stray current corrosion  
 4.8 Corrosive wear  
     4.8.1 Abrasive wear  
     4.8.2 Adhesive wear  
     4.8.3 Erosive wear  
     4.8.4 Fretting wear  
     4.8.5 Evaluating corrosive wear  
 4.9 Thermogalvanic corrosion  
 4.10 Intergranular corrosion  
 4.11 Environmentally assisted cracking (EAC)  
     4.11.1 Stress corrosion cracking (SCC)  
     4.11.2 Hydrogen embrittlement (HE)  
     4.11.3 Sulfide stress cracking (SSC)  
     4.11.4 Corrosion Fatigue (CF)  
     4.11.5 Liquid metal embrittlement (LME)  
 4.12 Photo corrosion

UNDERSTANDING CORROSION

M&N



### Understanding corrosion from an applied perspective

Theory and praxis

by Per Møller & Lars Peter Nielsen

Slide 20 - New Corrosion book, *Understanding Corrosion from an Applied Perspective*.



## NASF SURFACE TECHNOLOGY WHITE PAPERS

### 82 (12), 1-38 (September 2018)

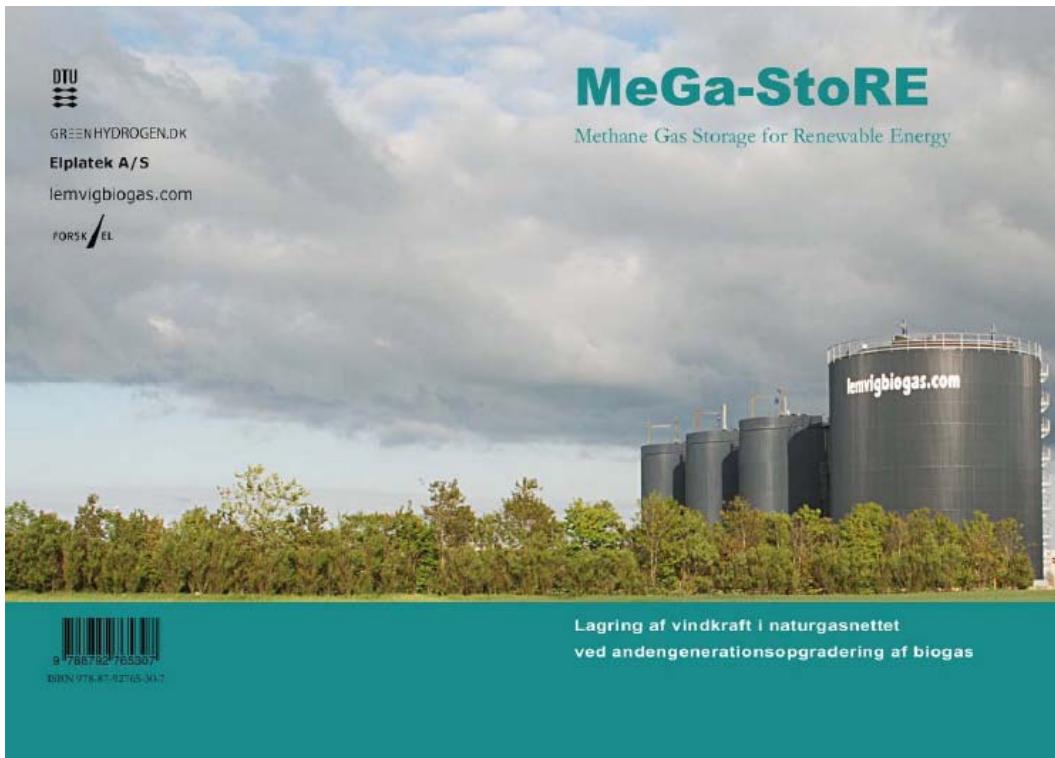
#### Methane gas storage for renewable energy (MeGa-StoRE)

Sustainable energy is a hallmark of the power profile in Denmark. Dr. Møller's work in this area has contributed to a program called MeGa-StoRE (Slide 21), where wind energy is converted to methane gas and stored in the country's natural gas grid.

At present, about 40% of Denmark's electrical supply is provided by wind turbines (Slide 22), with plans to exceed 50% by 2020-21. Wind turbine technology has advanced over the years, with the power generated by an individual unit continuing to increase (Slide 23). Denmark is a net exporter of energy when the wind is above a certain level.

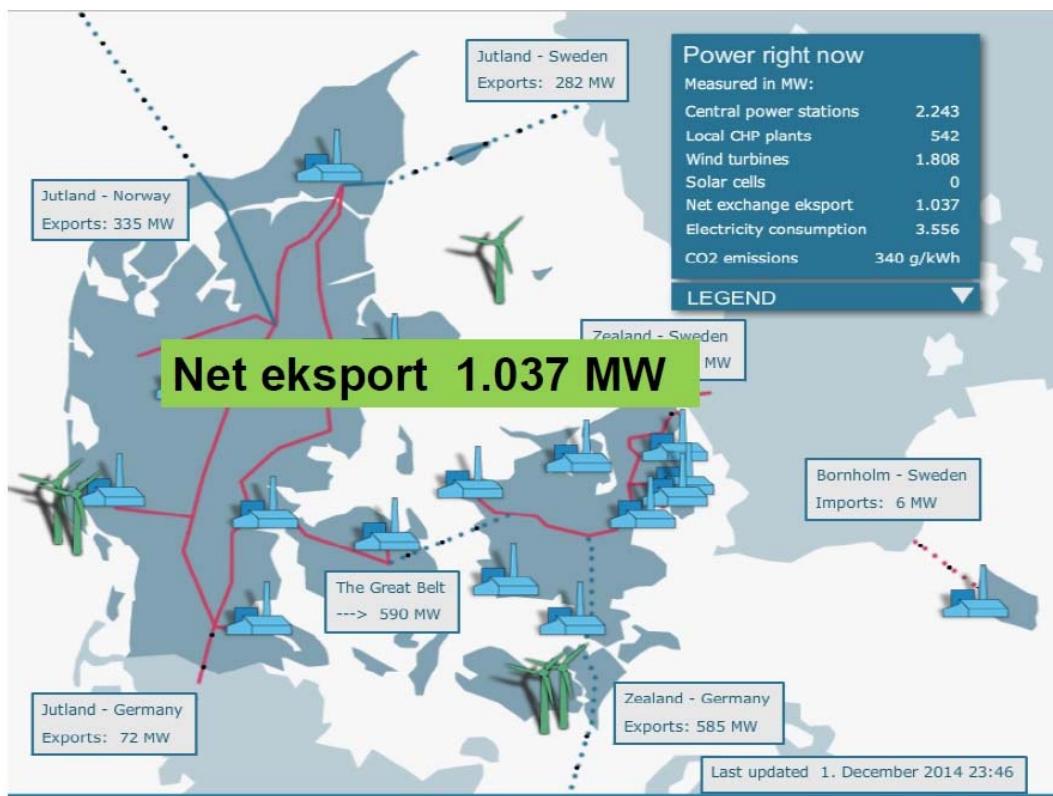
At the same time, biogas is extensively used as an energy source. Consisting of methane and carbon dioxide, thermophilic biogas is produced from waste generated by farms (manure) and industrial waste products.

Using electrocatalysis via alkaline electrolysis, Dr. Møller has developed the means of converting the wind energy from turbines into hydrogen (Slide 24). In turn, the hydrogen is reacted with the carbon dioxide in biogas to produce chemically pure methane. Virtually all of the CO<sub>2</sub> can be converted, and the methane is stored in the natural gas grid. Thus, excess wind energy, via hydrogen generation, is used to eliminate CO<sub>2</sub> in biogas and produce methane, for clean carbon-based energy. The concept has been proven at the Lemvig biogas plant, the largest in Denmark.



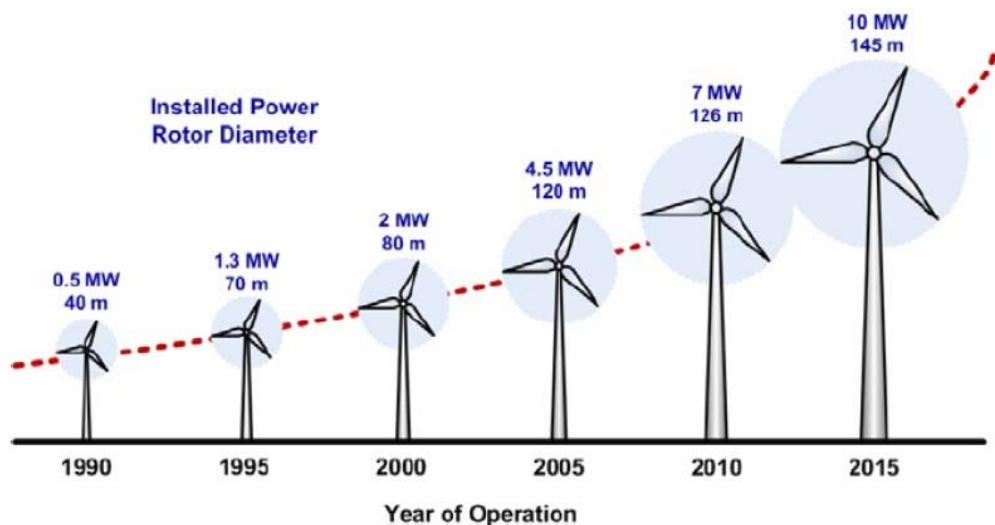
Slide 21- Methane gas storage for renewable energy.

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Slide 22 - Power profile in Denmark.

## Energy: Electricity, upgrading and conversion



Slide 23 - Growth in individual wind turbine power capacity (1990-2015).

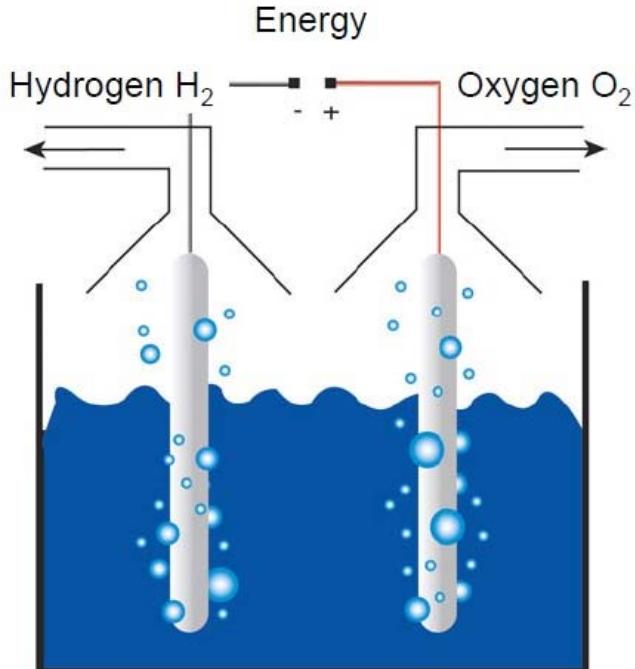
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### *Hydrogen generation - electrode development*

The key to the generation of hydrogen from wind energy (Slide 24), lay in the development of the catalytic electrode. Reaching back nearly 90 years, Dr. Møller found a 1927 patent (US Patent 1,628,190, *Method of Producing Finely Divided Nickel*), which provided the basis for the hydrogen generation (Slide 25). Finely-divided nickel, with very high surface area, was found to be extremely catalytic for hydrogenation processes. The preparation involves the mixing of nickel and aluminum, heating to form an alloy, and then selectively dissolving the aluminum, resulting in highly porous (*i.e.*, "finely-divided") nickel.

## Cheap hydrogen = winning position



25 wt% KOH at a temperature of 90°C

Slide 24 - Innovation in hydrogen generation.

## NASF SURFACE TECHNOLOGY WHITE PAPERS

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Patented May 10, 1927.

1,628,190



### UNITED STATES PATENT OFFICE.

MURRAY RANEY, OF CHATTANOOGA, TENNESSEE.

METHOD OF PRODUCING FINELY-DIVIDED NICKEL.

No Drawing.

Application filed May 14, 1926. Serial No. 109,169.

This invention relates to a method of preparing catalytic or finely divided material.

The principal object of the invention is the production of metallic nickel in a catalytic state such as may be used in the hydrogenation of oils, fats, waxes and the like.

To this end the invention contemplates the alloying of metallic nickel with metals such as silicon and aluminum in various proportions, and then dissolving the aluminum and silicon from the alloy by means of a solvent which will not attack the nickel, whereupon the nickel remains in a finely divided state.

In this condition the nickel may be extremely catalytic, these properties apparently being intensified by the treatment.

the invention is not to be restricted to the proportions given.

The solvent may be of any desired strength, dependent upon the rapidity with which it is desired to remove the aluminum, or the aluminum and silicon. In the dissolving action a considerable amount of hydrogen is liberated, and this may be saved and used for other purposes, or not, as found convenient and expedient.

After having dissolved out the aluminum

the aluminum and silicon from the resultant alloy.

4. A method of preparing a catalytic material which includes the step of alloying 50% nickel, 40% silicon, and 10% aluminum, and dissolving the silicon and aluminum from the resulting alloy.

5. A method of preparing finely divided nickel which includes the step of alloying 30% nickel, 60% silicon, and 10% aluminum and dissolving the silicon and aluminum from the resultant alloy and separating the finely divided nickel from the supernatant liquid.

In testimony whereof, I affix my signature,

MURRAY RANEY.

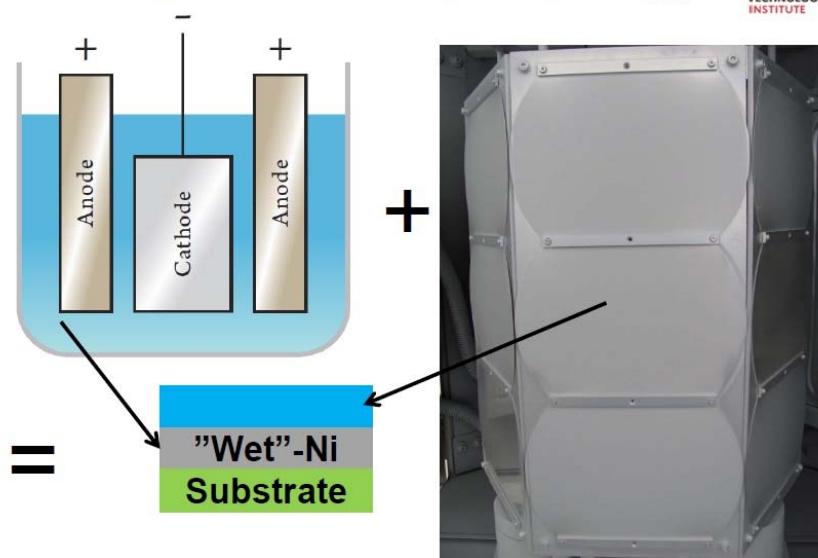
From 1926/1927

**Mixing Al and Ni + heating + dissolution of Al**

Slide 25 - U.S. Patent for producing finely-divided nickel.

The desired electrode was produced by a combination of physical vapor deposition and electrodeposition. Nickel was electrodeposited, followed by a PVD coating of aluminum (Slide 26). Slide 27 shows the nickel operation on a pilot scale, while Slide 28 shows the PVD operation. Alloying the layers at about 620°C produces a multitude of Ni-Al intermetallics, as in the phase diagram of Slide 29. The annealing process yields a distribution of Ni-Al phases, with  $\text{Ni}_2\text{Al}_3$  constituting the primary intermetallic in the bulk of the deposit near the surface (Slide 30). Finally, the aluminum was selectively leached from the  $\text{Ni}_2\text{Al}_3$ , resulting in an extremely porous nickel, ideal for electrocatalysis (Slides 31-32, by optical and electron microscopy, respectively)). Recent developments have improved the electrodes even further and a new solution based on electrodeposition only is being explored (Slide 33).

### Combining PVD and Electroplating



Slide 26 - Production of catalytic electrode by PVD and electroplating.

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## Combining PVD and Electroplating



Slide 27 - Electrodeposition of nickel.

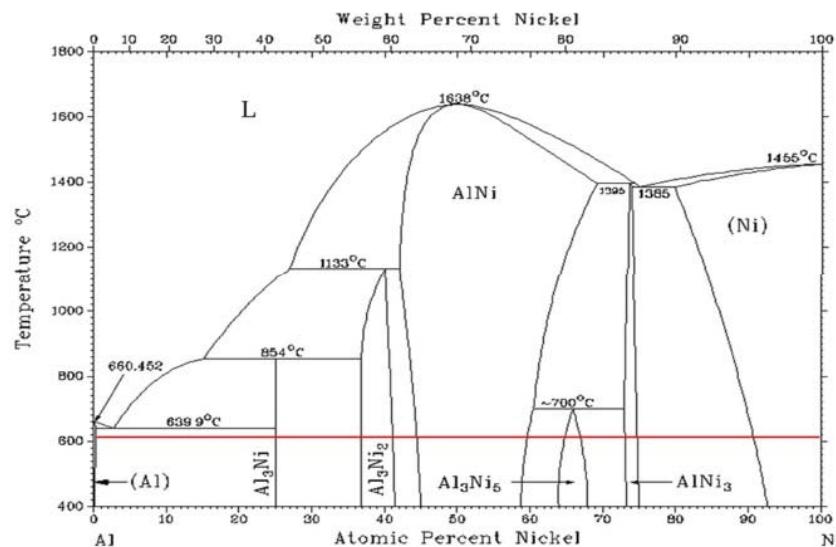
## Combining PVD and Electroplating



Slide 28 - Physical vapor deposition of aluminum.

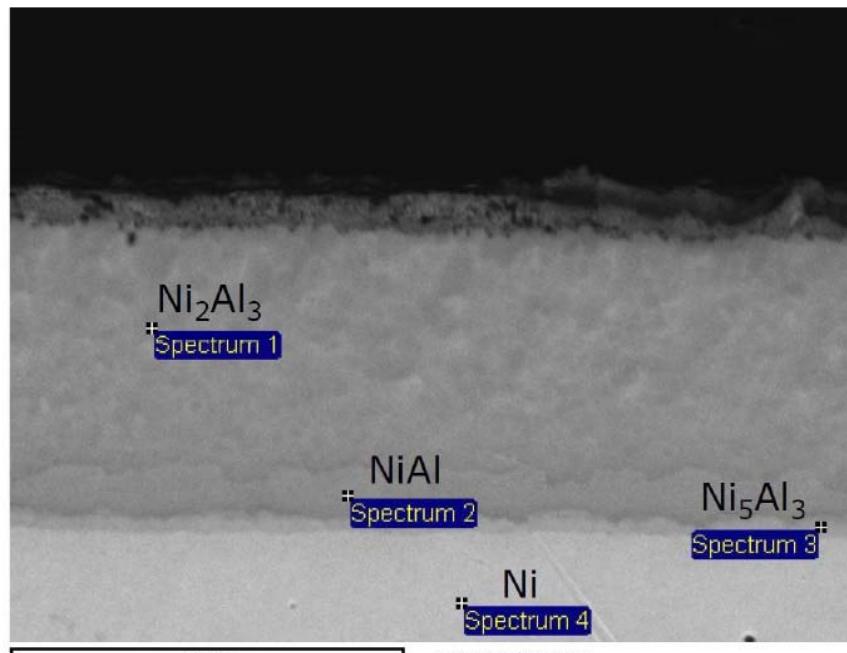
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## Combining PVD and Electroplating



Slide 29 - Nickel-aluminum phase diagram.

## Combining PVD and Electroplating

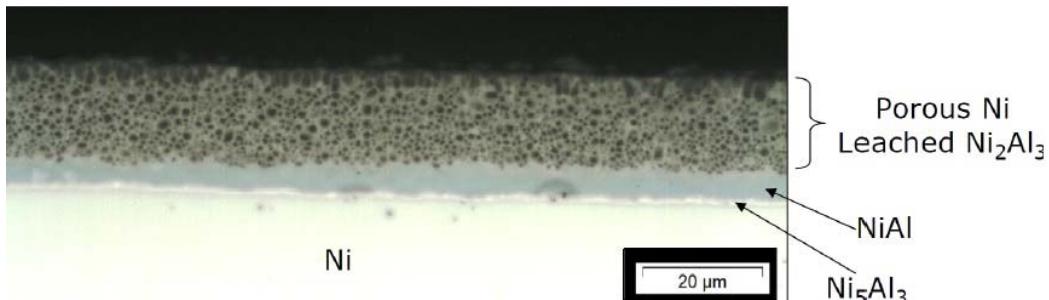


Slide 30 - Phase distribution in alloyed nickel-aluminum.

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## Combining PVD and Electroplating

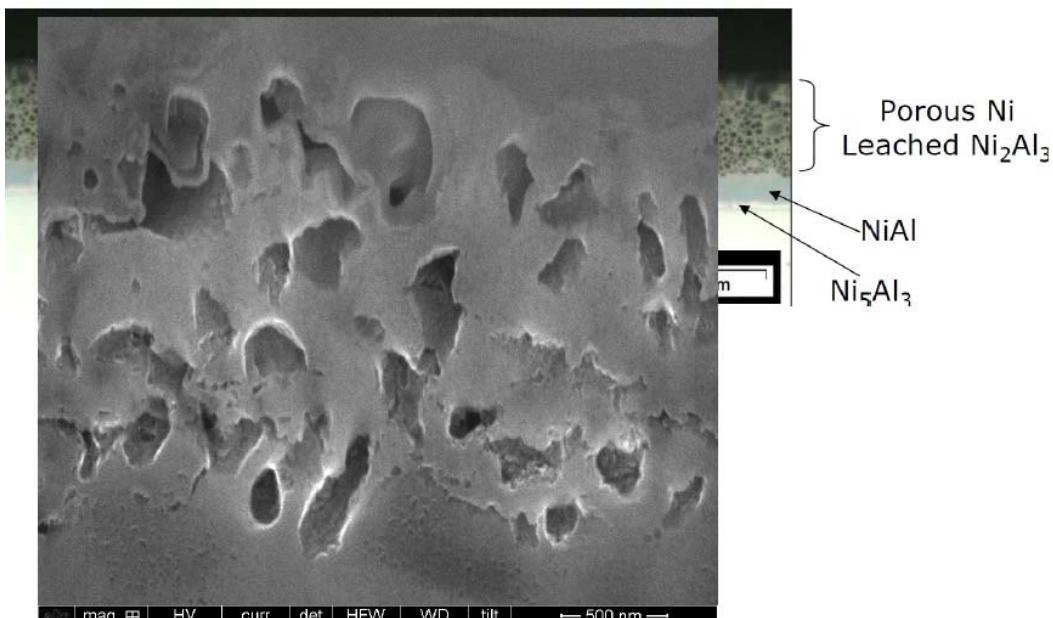
- Aluminum was selectively leached from the Ni-Al phase



Slide 31 - Optical microscopy: Aluminum selectively leached from  $\text{Ni}_2\text{Al}_3$ .

## Combining PVD and Electroplating

- Aluminum was selectively leached from the Ni-Al phase



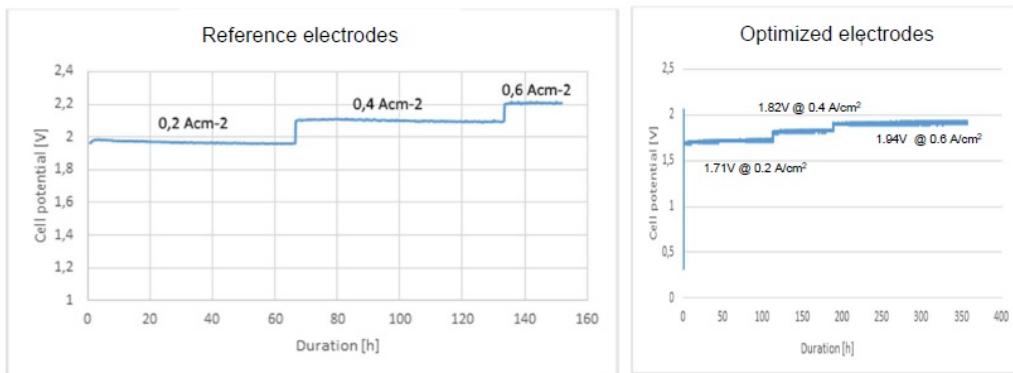
Slide 32 - SEM: Aluminum selectively leached from  $\text{Ni}_2\text{Al}_3$ .

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## New solution based on electroplating only...



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0.2 A/cm<sup>2</sup>: ΔU app. 0.2 V

0.4 A/cm<sup>2</sup>: ΔU app. 0.3 V

0.6 A/cm<sup>2</sup>: ΔU app. 0.3 V

Slide 33 - Electrode manufacture via electrodeposition only.

### Hydrogen generation - scale-up

Recent work has been involved in scaling up the hydrogen generation process. The nickel electrode plating operation shown in Slide 34 illustrate the scale of operation currently achievable.

### Upscaling based on electroplating

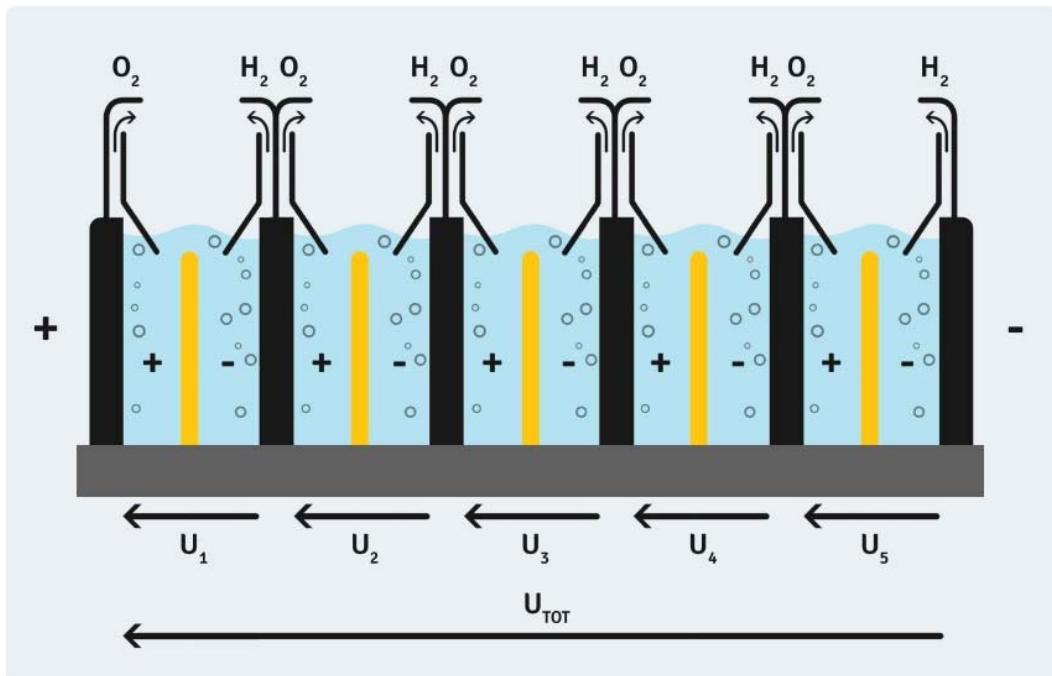


Slide 34 - Electrode scale-up.

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Using a bipolar principle, an array of electrodes connected in series allows production of hydrogen at significant rates (Slide 35). A full-scale unit (Slide 36) will be ready for testing in September 2018.



Slide 35- Schematic diagram of a full-scale hydrogen generation unit.

Testing will be initiated in September



Slide 36- Elplatek/HydrogenPro hydrogen production unit to be tested in September 2018.

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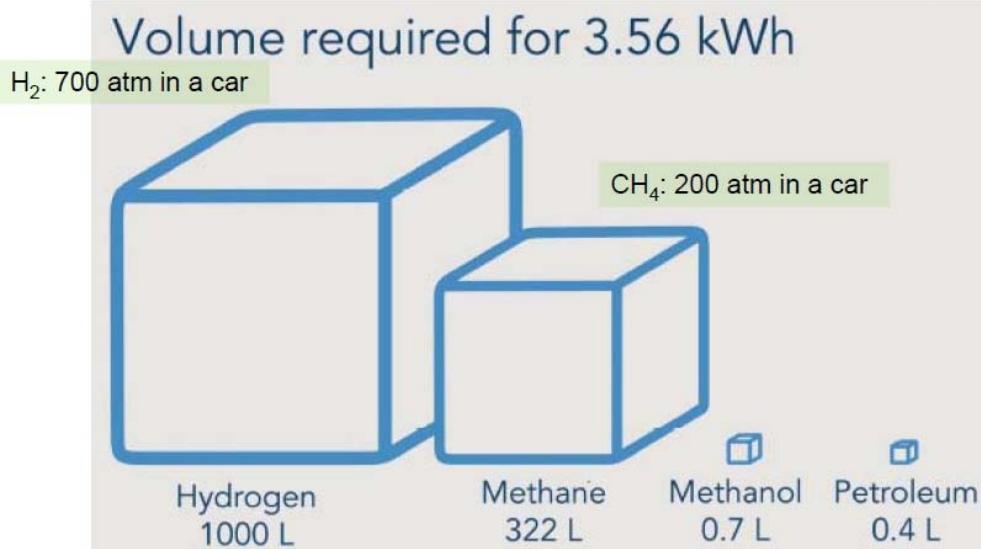
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### Potential for fuels

There are many aspects to the wind power-hydrogen-methane-biogas scheme that could be exploited. Among these was the potential for sustainably synthesizing fuels. If one considers the energy density of the substances considered here, it is obvious that the storage volume is critical for vehicles (Slide 37). Using an energy yardstick of 3.56 kW/hr between refueling, hydrogen would occupy 1000 L, requiring 700 atmospheres of compression to fit into a car realistically, a concept not too realistic in itself. Similarly, the methane equivalent would be 322 L, requiring 200 atmospheres of compression. However, methanol (not the ethanol used in cars in the United States) derived from methane, would occupy 0.7 L at one atmosphere. This compares with 0.4 L for petroleum at one atmosphere. Methanol would not be unrealistic.

In this way, Dr. Møller and his team envisioned the hydrogen produced by electrocatalysis from wind energy, being used to clean the biogas, thereby producing methane by reacting with the CO<sub>2</sub> in the biogas. The methane could then be converted to methanol by dry/wet reforming (Slide 38). He calculated that the energy content in the original biogas could be increased by 50% with this system (Slide 39).

### Energy densities



### Optimal to go for methanol production

Slide 37 - Comparison of potential sustainable fuels.

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## Modularized fuel factories



- Hydrogen production

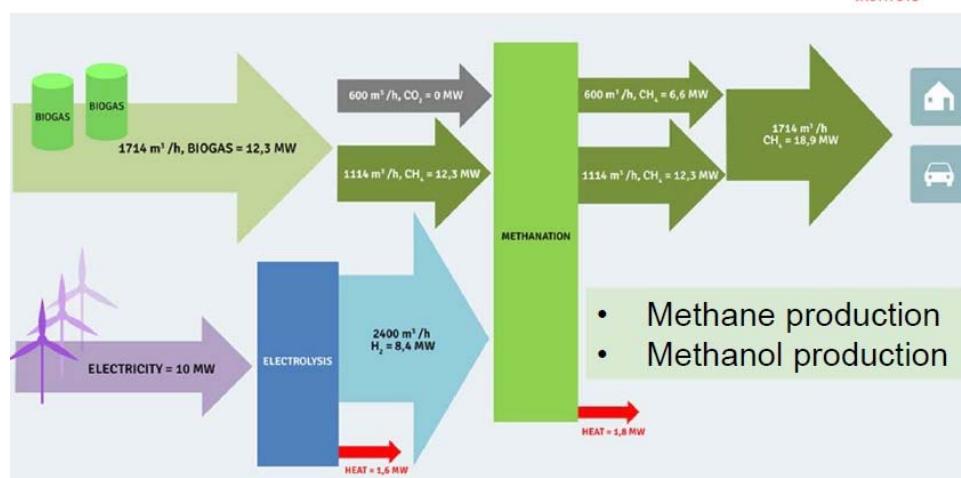


- Biogas cleaning



- Making methane by upgrading CO<sub>2</sub> in biogas to CH<sub>4</sub>
  - Making methanol by dry/wet reforming
- Slide 38 - Modularized fuel factories.

## Cheap hydrogen = winning position



**Upgrading biogas with hydrogen produced from wind turbines, the energy content in biogas is increased by 50%.**

Slide 39 - Energy enhancement of biogas to produce methane and methanol.

### Electrocatalytic cleaning of biogas

Given its origins, *i.e.*, farm and industrial waste, biogas is not pure in any sense. Although it consists of 65% methane and 35% CO<sub>2</sub>, there are significant impurities (Slide 40). Of significant note is sulfur, in the form of 2000 ppm of hydrogen sulfide and, to a lesser extent, 50 ppm of methanethiol. To be useful for further catalytic conversion, the sulfur must be removed. In conventional

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cleaning of biogas, there are still waste considerations (Slide 41). Although the H<sub>2</sub>S is effectively reduced from 2000 ppm to about 10 ppb, the sulfur is tied up as a metallic sulfide, which must be hauled away.

An electrocatalytic process was developed by Dr. Møller and his colleagues, which converts the sulfide in the biogas to pure sulfur, which can be used commercially (Slides 42-43). There is no resultant waste. Instead, the sulfur impurity can be put to use.

### Electrocatalytic cleaning of BioGas



#### What is biogas?

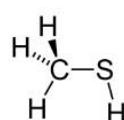
About 65 % methane CH<sub>4</sub>

About 35 % CO<sub>2</sub>

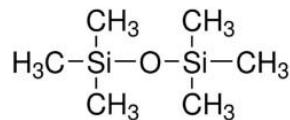
**About 2000 ppm H<sub>2</sub>S**

About 50 ppm methanethiol (CH<sub>4</sub>S)

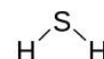
About 30 ppm hexamethyldisiloxane C<sub>6</sub>H<sub>18</sub>Si<sub>2</sub>O



methanethiol



hexamethyldisiloxane

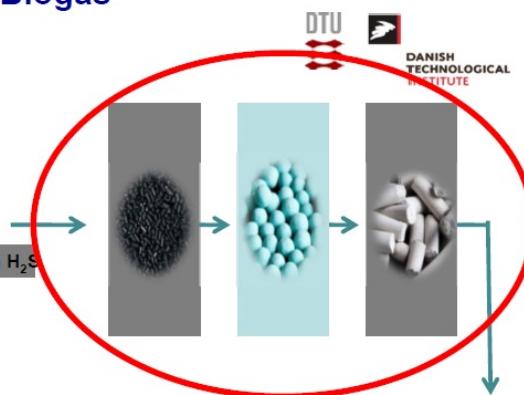


hydrogen sulphide

Slide 40 - Composition of biogas.

### Conventional Cleaning of Biogas

#### - what about waste?



Slide 41 - Waste considerations in conventional cleaning of biogas.

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## Electrocatalytic cleaning of BioGas



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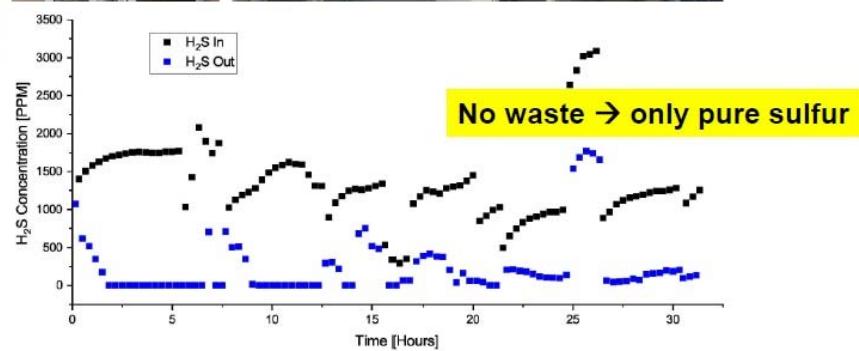


Slide 42 - Unit for electrocatalytic cleaning of biogas.

## Electrocatalytic cleaning of BioGas



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Slide 43- Impact of electrocatalytic cleaning of biogas.

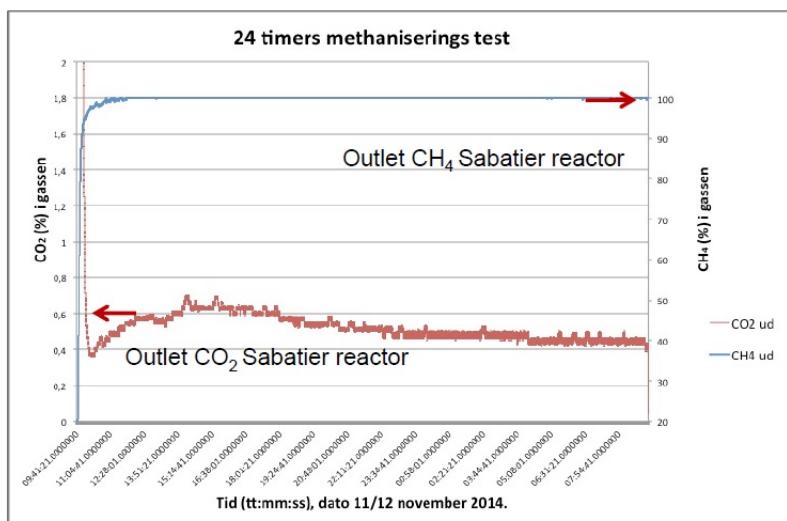
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#### *Production of methane and methanol*

As noted earlier (Slide 39), the next phase of this renewable energy system is the conversion of CO<sub>2</sub> to methane. The process uses the Sabatier reaction. Once again using the hydrogen from the wind-driven electrocatalysis, reaction with the carbon dioxide in the biogas produces methane and water. This requires a nickel catalyst (Slide 31) at a reaction temperature of 300 to 400°C (Slide 44). Such reactors, shown in Slides 45-46, are available on a commercial scale. Ultimately, the methane is converted to methanol fuel (Slide 47).

#### Upgrading CO<sub>2</sub> to CH<sub>4</sub> – 1 step Sabatier reactor



Slide 44 - Upgrading CO<sub>2</sub> to methane - Sabatier reactor.

#### Upgrading CO<sub>2</sub> in Biogas to CH<sub>4</sub>



Slide 45 - Upgrading CO<sub>2</sub> to methane - Pilot reactor.

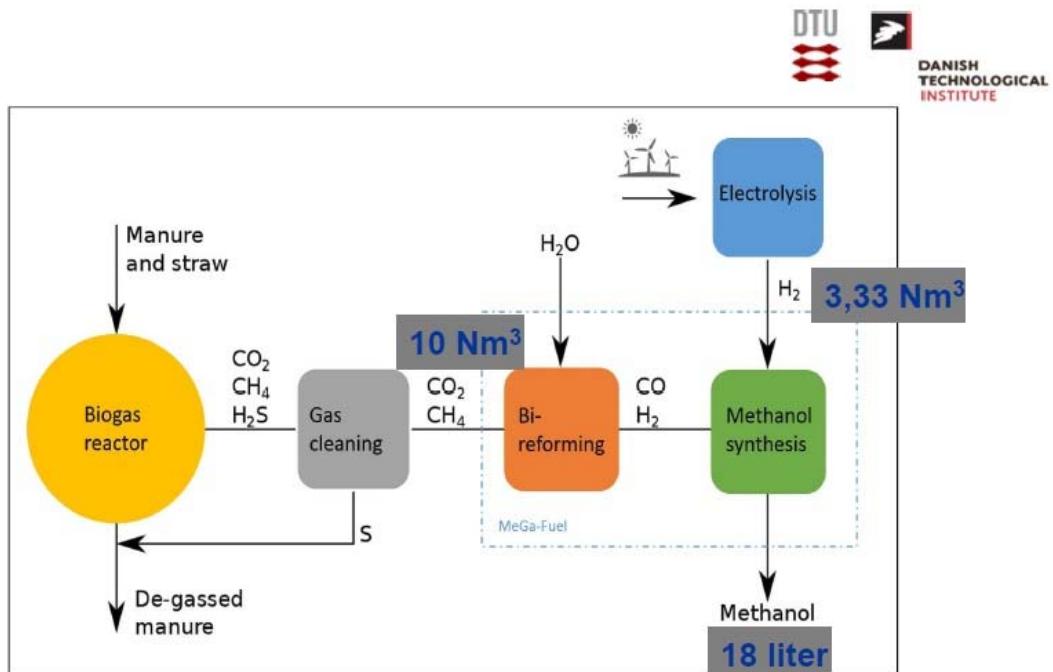
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## Upgrading CO<sub>2</sub> in Biogas to CH<sub>4</sub>



Slide 46 - Upgrading CO<sub>2</sub> to methane - Commercial reactor.

In summary, the overall strategy for this renewable energy concept is shown in Slide 47. The biogas derived from organic waste, once cleaned for sulfur (in pure form), yields CO<sub>2</sub> and CH<sub>4</sub>. The hydrogen derived from wind-driven electrolysis is then combined to synthesize methanol.



Slide 47 - Overall concept of extracting sustainable energy from wind power and biogas.

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*Methanol as a fuel*

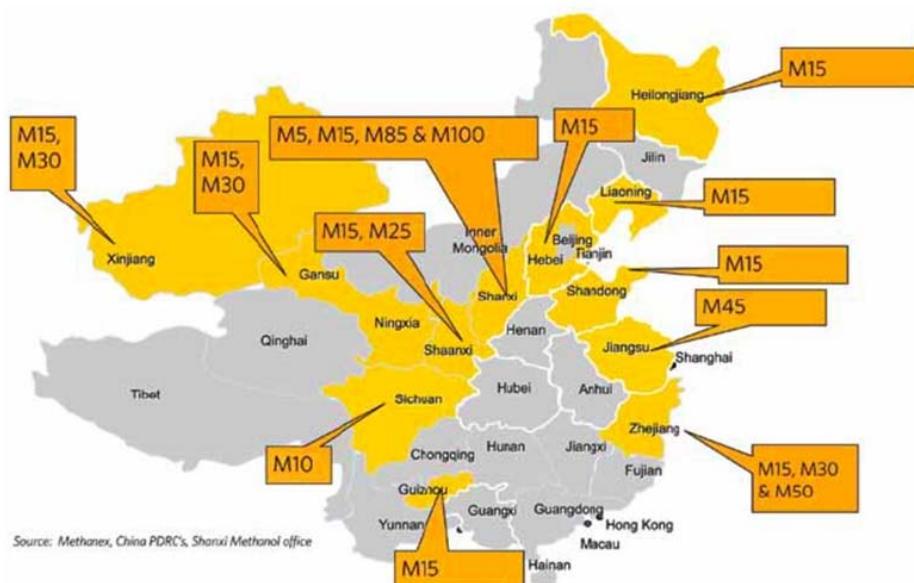
In North America, attention on alternative automotive fuels has been focused on ethanol. However, methanol has often been used in automotive racing, and is the focus in other areas of the world (Slide 48). Indeed, methanol is widely used in China (Slide 49). It is entirely reasonable to expect that wider use of this fuel offers a sustainable alternative fuel for the future.

## Driving on methanol



Slide 48 - Commercially-available methanol fuel.

## Methanol used in China



Slide 49 - Distribution of methanol fuel in China.

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Dr. Møller's work in this area has been rather significant. Indeed, it has gotten play in the newspapers in Denmark (Slide 50). In English, (via a loose computer translation), the headline reads, "How to get a jumbo jet to fly on wood alcohol."

## Politic commitment and action



Slide 50 - Reaction to Dr. Møller's work in Denmark.

## Self-cleaning paints

Another avenue of surface research has led Dr. Møller to look at self-cleaning paints. Such a paint would be hydrophobic and oleophobic, repelling both water and oils, respectively. The paint would continue to maintain this property even after scratching or scuffing. It would keep pollen, insects, stains, etc., from sticking to the surface.

It was found that titanium dioxide is widely used as a pigment in paints, cosmetics, etc. Anatase, a tetragonal form of  $\text{TiO}_2$  - the others being rutile, the most common form, and brookite, an orthorhombic form - possesses photocatalytic surface properties. Photoactive titania in the form of anatase was seen as a means of forming a self-cleaning surface, in addition to several other applications (Slide 51).

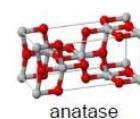
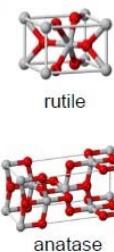
Slide 52 shows the performance of a normal paint, and a self-cleaning one, containing anatase, before and after exposure to 28 hr of UV. As can be seen, the blue stain on normal paint is unaffected, while it disappears from the surface of the self-cleaning paint.

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## Self-cleaning paint, TiO<sub>2</sub>



- Polymorph material: rutile, anatase, brookite
- Widely used as pigmentation in paint, cosmetics, food, ...
- Photocatalytic properties (anatase) discovered in 1967
- Possible industrial applications of photoactive titania coatings:
  - 'Self-cleaning' surfaces
  - Water purification, air cleaning
  - Antibacterial, antimicrobial, fungicidal properties
  - Hydrophilic surfaces
  - Photovoltaics

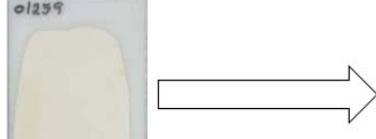


Slide 51 - Basis for titania in self-cleaning paints.

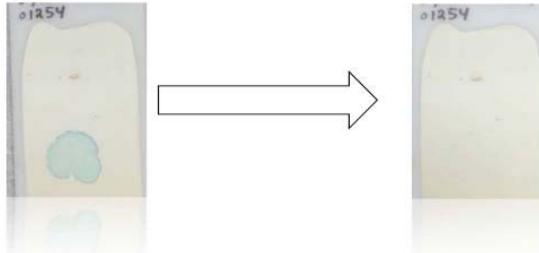
## Self-cleaning paint



Normal paint



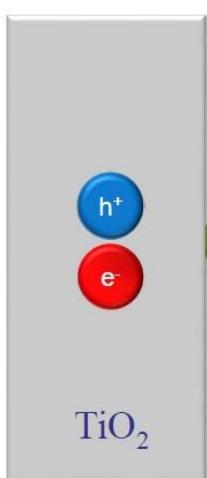
Self cleaning paint



Slide 52 - Laboratory performance of self-cleaning paint.

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## Integrating $\text{TiO}_2$ into paint



- $\text{TiO}_2$  mixed into paint
- Anatase/ $\text{TiO}_2$  absorbs energy from the sunlight and creates electron/holes and OH radicals
- OH radicals break down organic matter
- What happens to the paint?



Slide 53 - Integrating titania into paint: (1) the concept.

When anatase is mixed in with the paint, its photoactive surface absorbs the energy from the sunlight, creating electron holes and  $\text{OH}^{\cdot}$  radicals (Slide 53), which in turn break down the organic matter forming  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

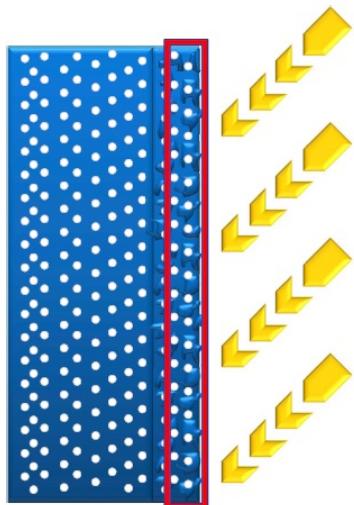
When nano-sized  $\text{TiO}_2$  particles are mixed into the paint (Slide 54), the contact area between the organic binder material and the particles is extremely high. At the surface, the binder is affected by the photocatalytic reaction, resulting in a massive release of  $\text{TiO}_2$  from the surface. Thus, an organic binder cannot be used, as it leads to poor durability, and the usual unsightly chalking occurs.

The solution to this problem was the use of  $\text{TiO}_2$ -coated glass beads (Slide 55). The beads are deeply imbedded into the film and do not fall out. There is considerably less direct contact between the  $\text{TiO}_2$  and the binder. As a result, minimal organic binder is affected by the photocatalysis, and a long lasting, self-cleaning film is obtained.

Dr. Møller has worked with a commercial paint manufacturer to perfect the incorporation of  $\text{TiO}_2$  in the matrix via a patented process (Slide 56-57). An atomic layer deposition (ALD) process in a specially constructed reactor converts titanium chloride ( $\text{TiCl}_4$ ) to  $\text{TiO}_2$  at exceedingly small thicknesses on the glass bead surface (20-30 nm). The result is a self-cleaning paint of high durability.

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## Integrating $\text{TiO}_2$ into paint

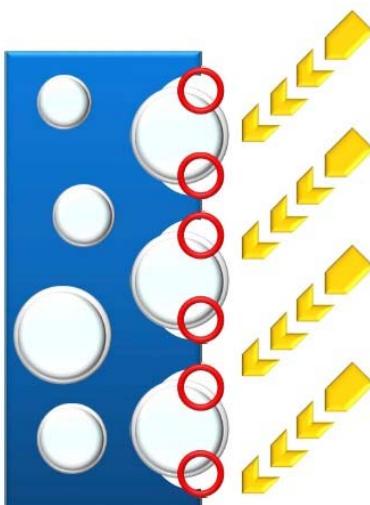


- $\text{TiO}_2$  mixed into paint
- Contact area between binder and  $\text{TiO}_2$  nano-particles extremely high
- All the binder at the surface is affected by the photocatalytic reaction
- High release of  $\text{TiO}_2$  particles
- Impossible to use organic binder
- Poor durability
- Chalking and loss of gloss/color



Slide 54 - Integrating titania into paint: (2) by mixing.

## $\text{TiO}_2$ coated spheres into paint



- $\text{TiO}_2$  coated spheres:
- Much less contact between binder and particles
- Small amount of binder at the surface is effected by the photocatalytic reaction
- Glass beads are embedded deeply in the film and do not fall out
- No release of nanoparticles
- Long lasting film with long lasting self cleaning effects



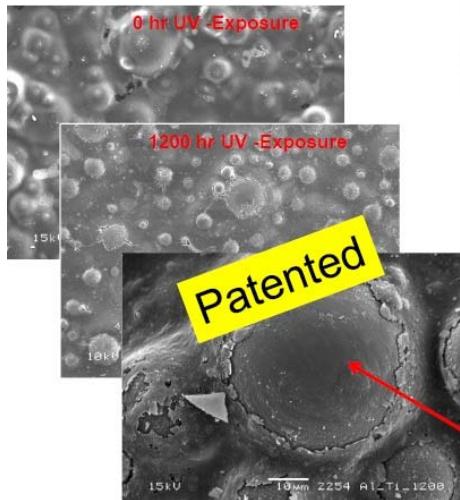
Slide 55 - Integrating titania into paint: (3) using  $\text{TiO}_2$ -coated spheres.

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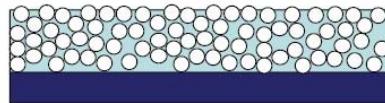


High durability & self-cleaning



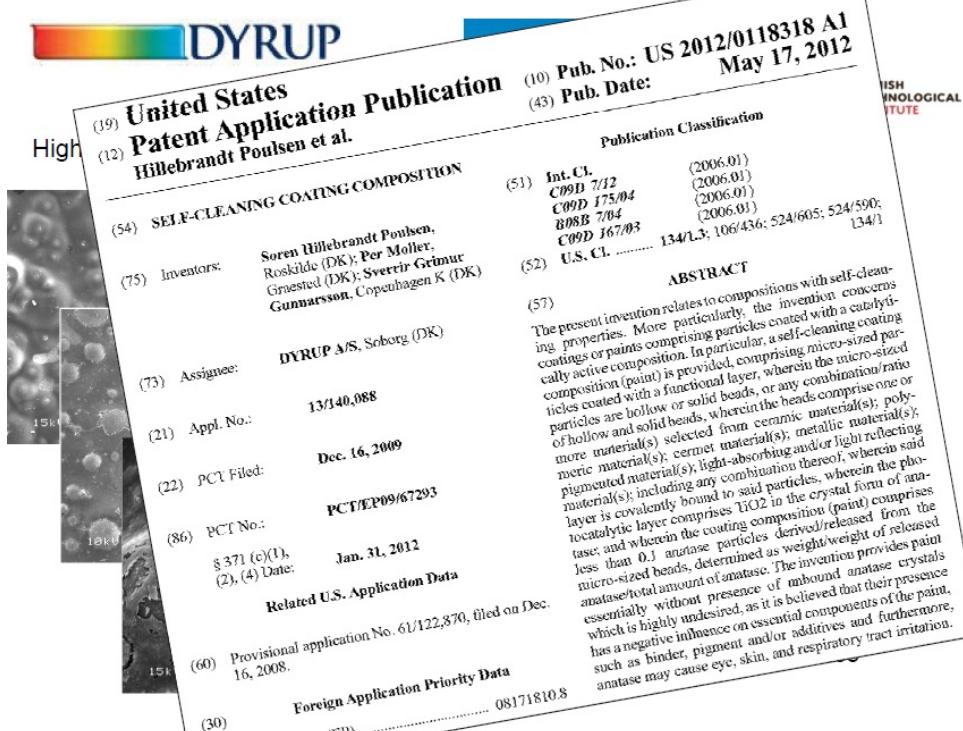
ALD (Atomic Layer Deposition)

Made by a cyclic process in a specially constructed reactor



20 - 30 nm TiO<sub>2</sub> at the surface

Slide 56 - Integrating titania into paint: (4) commercially available.



Slide 57 - Integrating titania into paint: (5) patented process.

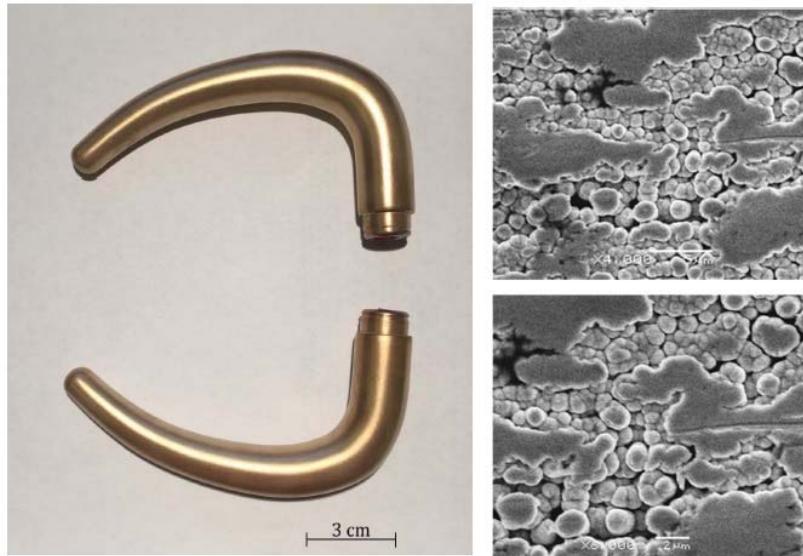
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#### Antibacterial Ag-Cu surfaces

Another part of Dr. Møller's work involves the development of antibacterial surfaces. Consider the common door handle in a public building, *e.g.*, a hospital, with hundreds of hands, containing oils and bacteria of unknown origin, ready to raise a public health issue at a moment's notice. The solution was a silver-copper alloy finish known to possess anti-bacterial properties (Slide 58). And again, news of this work became well known in the local papers (Slide 59). In English, (via another loose computer translation), the headline reads, "Door handle gives bacteria a fight to the finish."

#### Antibacterial Ag-Cu surfaces



#### Elplatek Electroplating technic

Ciacotich N. et al., Surface & Coatings Technology 2018

Slide 58 - Morphology of antibacterial Ag-Cu surface.

#### Antibacterial Ag-Cu surfaces



#### Dørhåndtag giver bakterier kamp til stregen

Virksomheden Elplatek og DTU samarbejder om bakteriedræbende dørhåndtag

Af Lotte Brechmann

**OVERFLADEBEHANDLING:** Et tre-årigt projekt har fokuseret på mindesmede overfladebehandlinger af håndtag i hospitalsmiljøer. Det er virksomheden Elplatek og Danmarks Tekniske Universitet, DTU, der nu er gået sammen om at udvikle en bakteriedræbende belægning til dørhåndtag.

- Det er en kobber- og svovlbelægning. Kobber og svovl er kendt hver for sig som stoffer, der kan have gode effekter, man ved, at kobber har bakteriehemmende egenskaber, og så kom tanken, hvad hvis man kombinerer kobber og svovl, fortæller Jan Boye Rasmussen, administrerende direktør i Elplatek.

Op de foreløbige resultater er gode. Laboratorieforsøg har vist, at kobber- og svovlbelægningen reducerer bakterier med mere end 99,9 procent allerede efter to timer eksponering på kobber-

„Det er virkelig noget, der gør en forskel

Jan Boye Rasmussen

solvoverfladen.

- Der er virkelig noget, der gør en forskel, siger Jan Boye Rasmussen.

Her i løbet af foråret bliver det bakteriedræbende dørhåndtag approvet i en lægepraksis. Og næste skridt er test på hospitaler.

Vi vil gerne have felsstudier på et par hospitaler, hvor vi kan undersøke, hvor meget det kobber- og svovlbelagde dørhåndtag reducerer bakterier i virkeligheden sammenlignet med almindelige dørhåndtag i rustfrit stål. Og vi forventer, at resultaterne fra vores laboratorieforsøg vil blive bekræftet af felsstudierne, fortæller ph.d.-studerende på DTU og

Elplatek, Nicole Ciacotich. Projektet er i øjeblikket på udvikling efter hospitalsafdelinger, der kunne se sig at være med til at teste dørhåndtaget.

**Store perspektiver**

Hvad ser I på perspektiver i projektet?

- Perspektivene er efter vores opfatning ganske store. For hvis lidt større og lidt mere udbredte tests fortæsser med at udvise de samme resultater, så er det en forholdsvis billig og overkommeleg måde at gøre en stor indsats på, lyder det fra Elplateks administrative chef.

Projektet har i første omgang fokus på hospitaler, men man kunne også forestille sig nogle andre områder, hvor et dørhåndtag med antibakteriel virkning kunne være interessant, fortæller han.

Elplatek og DTU er begge en del af Fast Track-partnerskabet, der også tæller Teknologisk Institut, For-

ce Technologi, Aalborg Universitet, Siemens, Hembel og Terning.

- Partnerne i Fast Track-sejruppen har så mange kompetencer, som vi aldrig selv ville have fået til at kunne komme i nærheden af som mindre virksomhed, oplyser han hurtigt fra spørgsmål, når der er behov for det, det har vært vært en synse for os, og der er også med til at kunne drive det fra projektet hurtigere frem, siger Jan Boye Rasmussen.

Det tre-årigte projekt, der løber frem til sommeren 2019, er støttet økonomisk af Innovationsfonden.

**Dørhåndtaget med kobber- og svovlbelægning er et led i et ph.d.-projekt, fortæller Nicole Ciacotich. Fotos: DTU.**

Slide 59 - News article on antibacterial-coated door handles.

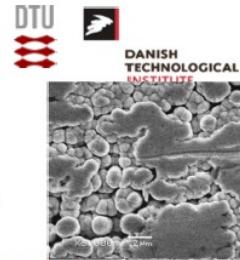
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The mechanism whereby the antibacterial action takes place depends on the alloy content and the presence of a porous microstructure capable of retaining moisture. When a bacterium makes contact with the Ag-Cu deposit, oxidation of the copper and the corresponding reduction of silver produces copper ions and hydroxyl ions on the surface, killing the organism (Slide 60).

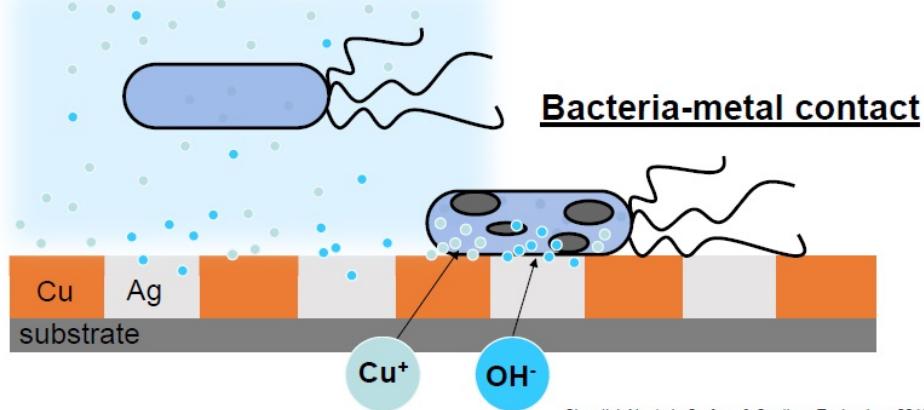
Testing involved the exposure of Ag-Cu coated test slides to a number of very common bacteria species to the contact killing mechanism (Slide 61). Dry conditions were specified, and re-inoculations of the bacteria on the test surface were undertaken every three hours for up to 21 hours, *i.e.*, multiple times. Success was defined as a minimum of 90% reduction in numbers of bacteria at all recovery times. The results were compared with tests on an uncoated 316 stainless steel reference surface. The results shown in Slide 62 indicate the effectiveness of the Ag-Cu surface in eradicating all types of bacteria tested with a killing rate of six to eight orders of magnitude. Slide 63 shows visual evidence, with the color changing from green (live bacteria) to red (dead bacteria) indicating extermination of the bacteria after 25 min. exposure to the Ag-Cu coating.

## Antibacterial Ag-Cu surfaces



### Galvanic coupling

- oxidation of Cu
- reduction on Ag
- porous microstructure
- cathodic/anodic area (silver/copper ratio content)



Slide 60 - Antibacterial mechanism.

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## Antibacterial Ag-Cu surfaces



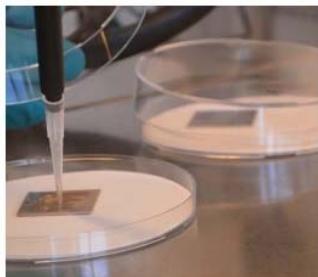
*Staphylococcus aureus* (ATCC 6538)

*Enterobacter aerogenes* (ATCC 13048)

*Pseudomonas aeruginosa* (ATCC 15442)

MRSA (ATCC 33592)

- Dry conditions
- Contact killing mechanism



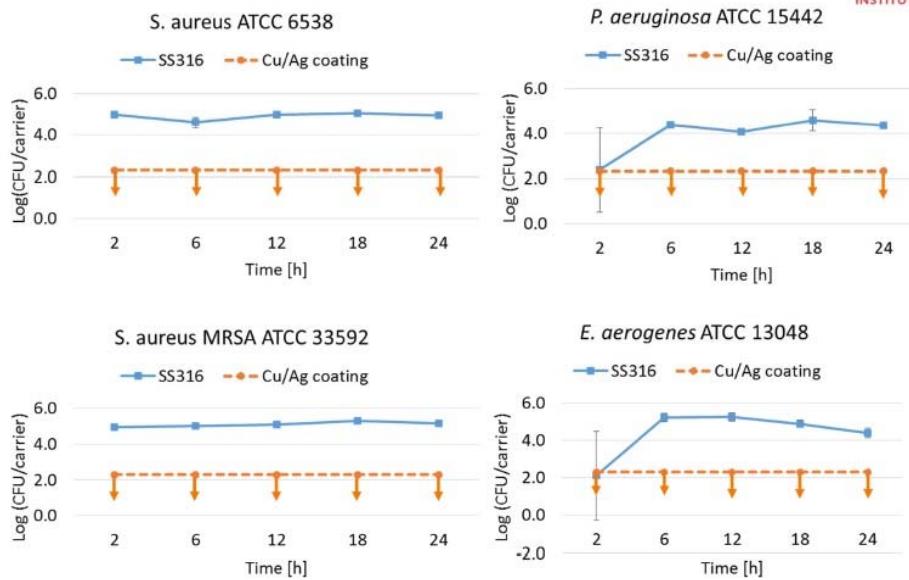
Re-inoculations after 3, 6, 9, 12, 15, 18 and 21 hours (1, 2, 4, 6 and 8 times)

Test performance criteria:  
Minimum of 90% reduction in numbers  
at all recovery times

Ciacotich N., Tesdorpf J. et al., manuscript in preparation

Slide 61 - Antibacterial test protocol.

## Antibacterial > 99.9% reduction

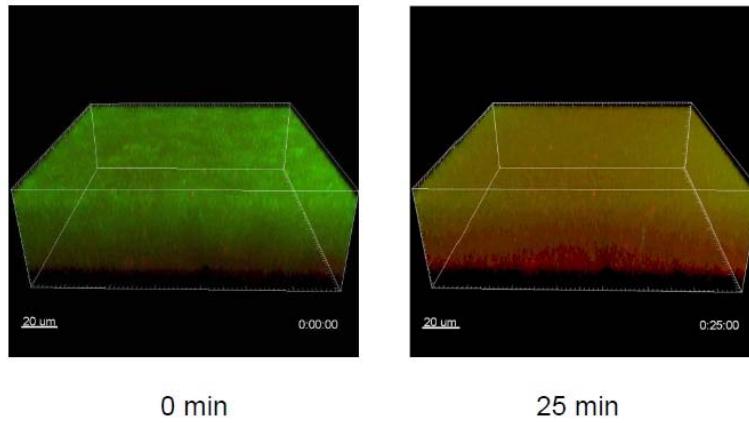


Ciacotich N., Tesdorpf J. et al., manuscript in preparation

Slide 62 - Antibacterial test results (1).

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## Antibacterial Ag-Cu surfaces



Slide 63 - Antibacterial test results (2).

### Summary

To sum up (Slide 64), Dr. Per Møller's work has covered a multitude of applications where surface technology is critical to success. In concert with his longtime colleague, Dr. Lars Pleth Nielsen, he has documented this work through patents, papers and renowned books. The scope of his work goes beyond the more common applications found in deposition. The sustainable energy scheme described on these pages, using the principles of electrocatalysis, promises to leverage the maximum amount of energy from wind power and biogas, the latter a resource that would otherwise be considered as pure waste in other times. The work with self-cleaning paints and antibacterial surfaces are other examples of novel applications requiring an understanding of electrochemistry and surface technology in real applications outside laboratory conditions which is indeed one of Dr. Møller's many skills.

### William Blum Lecture



Highlights of Prof. Per Møller's contributions to surface finishing:

- Patent examples
- Book examples
- New ideas connected to energy
- Electrodes for alkaline electrolysis, generating hydrogen
- Electrolytic cleaning of Biogas
- Methane and methanol formation
- Self-cleaning paints
- Antibacterial surfaces

We would like to invite you to collaborate with us

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Slide 64 - Summary



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### About the lecturers



**Professor Per Møller** has a Ph.D. in surface technology from the Technical University of Denmark (DTU), in Lyngby, Denmark. During the past 30 years, he has been engaged in contract research with industry covering nearly all aspects from micro-plating, under cleanroom conditions, to the design and implementation of industrial-scale electroplating lines. He is author or co-author of more than 135 scientific papers and holds more than 25 patents in the field of surface technology and electrochemistry. Currently, he is Professor in corrosion and surface technology at the MEK-DTU Section for Materials and Surface Engineering.



**Dr. Lars Pleth Nielsen** has a Ph.D. in Surface Science from Aarhus University (Denmark) and a managerial degree in Organization Management and Innovation from Copenhagen Business School. He has been employed as a Research Scientist at Haldor Topsøe and in the Photonic Group at NKT Research and Innovation A/S. Currently, he leads the Tribology Center at the Danish Technological Institute.