Aalto University

CHEM-E5145
Material durability

Workshop 3
24.1.2019

Annukka Santasalo
Annukka.santasalo@aalto.fi

Indentent learning outcomes
Workshop III

Discover the basics of common degradetion mechanisms in these applications → Identify common degradetion mechanisms in these applications

Share the expertise of ones field in a heterogenius team

Recognition why new material solutions are needed → Develop new material solutions and eco-designs

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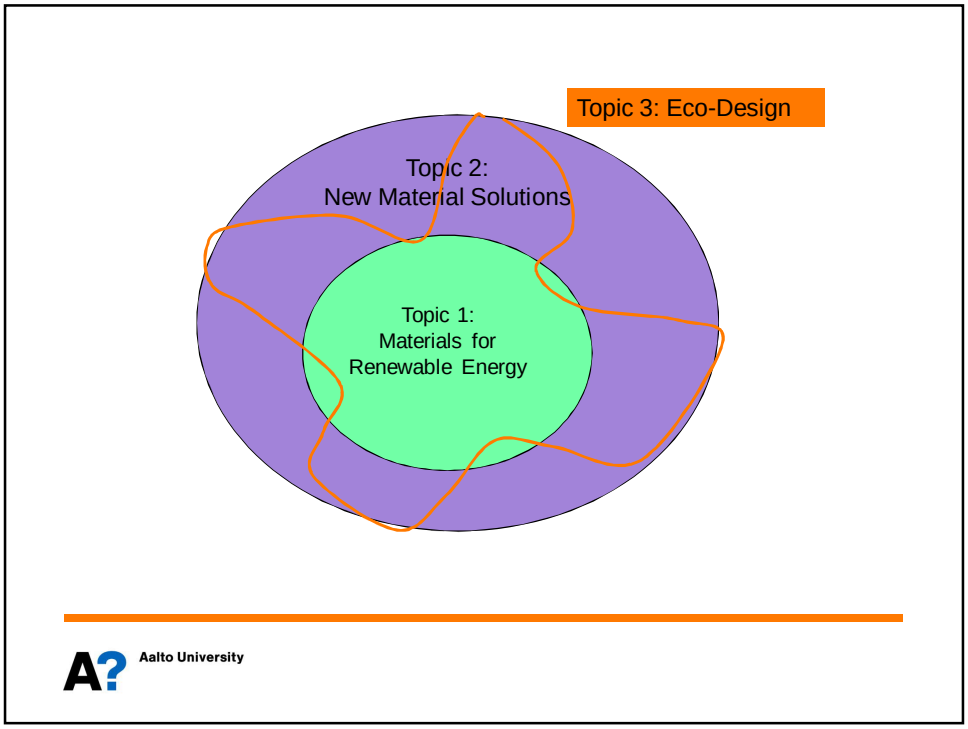

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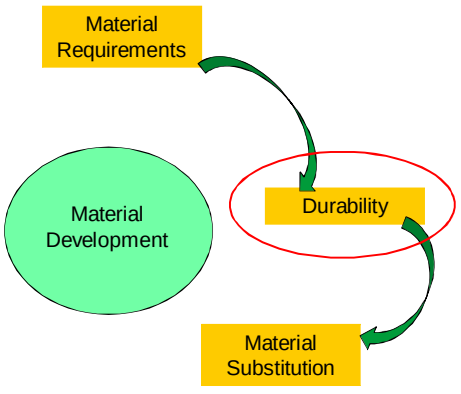
Topic 2 – New Materials Solutions



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Workshop timetable

- 8.30-9.30 poster preparation
- 9.30-10 gallery walk with posters
- 10-10.15 Sum-up the posters

  Break 15 min.

Workshop atmosphere 2016

- 10.30-11.15 Material durability

  Break 5 min.

- 11.20-11.45 Peer-review of Flip reports + videos preparation

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Important dates

- Task 3 presentations
  - **28.2 at 14-17**, the room will be announced later
    - If you are not able to join, there will be instructions later on
- Excursion to VTT
  - **14.2 at**
    - Team 1 13-14
    - Team 2 14-15
  - Registering at MyCourses (as I confirm the size of teams)
  - You are going to need identification with you (drivers license/passport)

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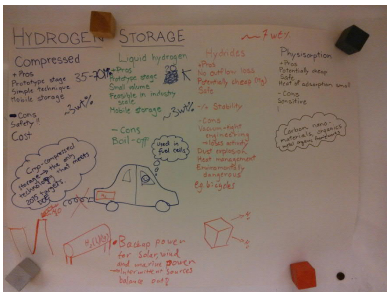
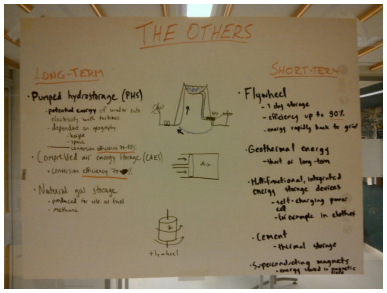
Flip Activity

New Material Solutions
In your Application





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Groups and Topics: Task 1 + 2

Group A
Off-Shore Wind
- Tuulia
- Katriina
- Veera
- Sai
- Konsta

Group B
Thermal Storage
- Marina
- Reima
- Riina
- Lucas
- Henna-Liisa

Group C
Flow Battery
- Henri
- Neea
- Veera
- Ella
- Marina

Group G
Solar PV
- Tomi
- Karim
- Irina
- Frej

Group D
Solid Oxide Fuel Cell
- Nikhil
- Jarkko
- Aino
- Judit
- Julia

Group E
Concentrated Solar Power
- Verna
- Hamidreza
- Anna
- Lillian
- Efran

Group F
Marine
- Alexandra
- Karri
- Jacopo
- Jyrki

Group I
"PEM electrolyser"
- Marko
- Sandesh
- Ahman

Flip Activity

- Poster tour
  - > Each of you will have your own team and you will teach the topic to others (5 min /poster)
  - Make questions, what did you not understand! (if not don't know – ask teacher or make a post-it tag to the poster
- Poster's and their presenting is evaluated
  - You all vote for the best poster (clear message)
  - The best posters get's automatically 4 p./workshop
  - Others get evaluated by the teachers 0-4 p. depending on the video posting (peers + teachers)

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Best Poster selection

Vote for the best poster!

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Sum up from the poster's

What were the materials that most of the new material solution were related on?

Were there any similarities between different applications?

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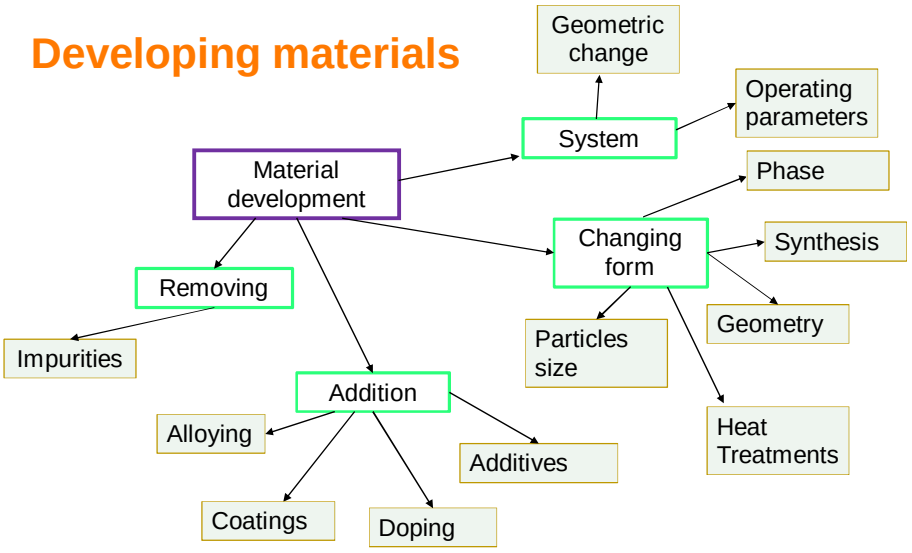
Developing materials



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Mind map 2018
New approaches?

Task 2

Brainstorming….

In your group:

New material solution

For next week

Identify:

- A material issue in your application
- Various possible solutions for that issue

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Task 2

Presenting at 7.2.2018 Workshop 5

Pitch your New Material Solution

3 min.

Innovate new ideas

Showing something from a any reference is failed

Has to be something that has not been tested at that application ever…

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Brainstorm in your group

What type of ideas for New Material Solutions
You have seen at the posters?
Or from literature you have read?

New Material Solution

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Process them at your own time

Break 15 min.

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Material Durability

Research

The DEN-RuO_2 significantly improves the cycling stability of Li-O_2 batteries with carbon electrodes and decreases the charging potential **even at ten times** less catalyst loading than those reported previously. [13866 hits]

Single-walled carbon nanotubes (SWCNT) are **novel material** with unique electronic and mech. properties. [2093]

Nitrogen-doped graphene has been demonstrated to be an excellent multifunctional material due to its intriguing features such as **outstanding** electrocatalytic activity… [45443]

high impact technologies [1215]

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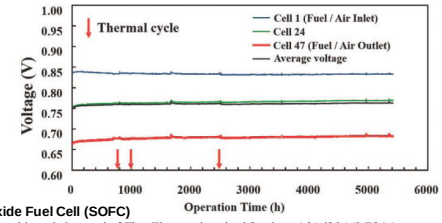
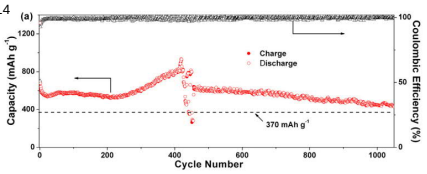
Durability
- close to market applications



Solid Oxide Fuel Cell (SOFC)
Y. Kobayashi et al. Journal of The Electrochemical Society,161 (2014) F214



Li-ion batteries
X. Zhang et al. / Journal of Power Sources 268 (2014) 365-371

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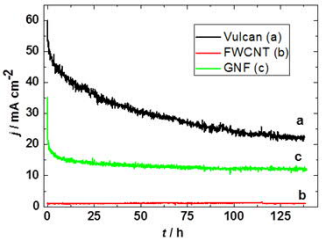
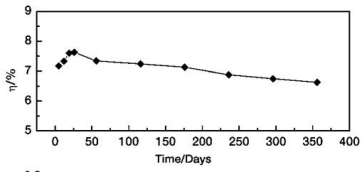
Durability
- early stage applications



Direct Methanol Fuel Cell 70 °C. A. Santasalo-Aarnio et al. Int. J. Hydr. Ene. 37 (2012) 3415.



Dye-senstitive solar cell, TiC/Pt counter electrode, Wu et al. J.Mater.Chem.A (2013), 1, 9672.

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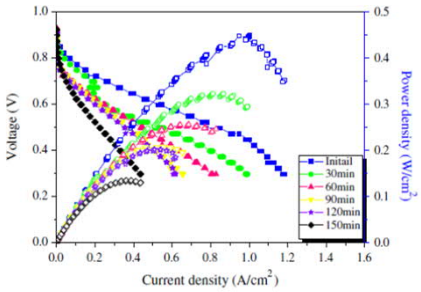
Accelerated tests for active materials

- To speed up the degradation
- Unrealistic conditions?

  -> What do these tell us?

Case: PEM FuelCell

At start-stop cycles a cell can Jump to 1.5 V (for seconds)
-> In this test they applied constant 1.5 V for 30 min. -> 150 min.



G.-B. Jung et al. Applied Energy 100 (2012) 81-86.

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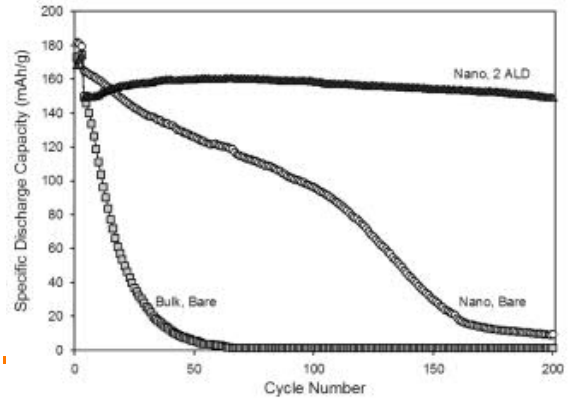
Are they useful?

Material degradation

- How much is accepted?
- When does the application become useless?

What is presented as reference data?



What do you think, do you trust this Bulk data?

$LiCoO_2$ anode material, I.D. Scott et al. "Ultrathin Coatings on Nano-LiCoO 2 for Li-Ion Vehicular Applications" Nano Letters 11 (2011) 414.

Discussion

- How often
  - Charge a mobile phone?
  - Change the solar panel of your summer cottage?
  - Change the fuel cell modules of your car?

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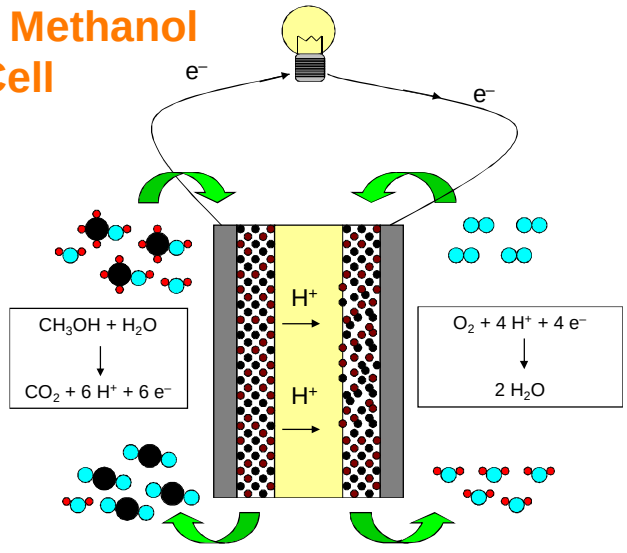
Direct Methanol Fuel Cell



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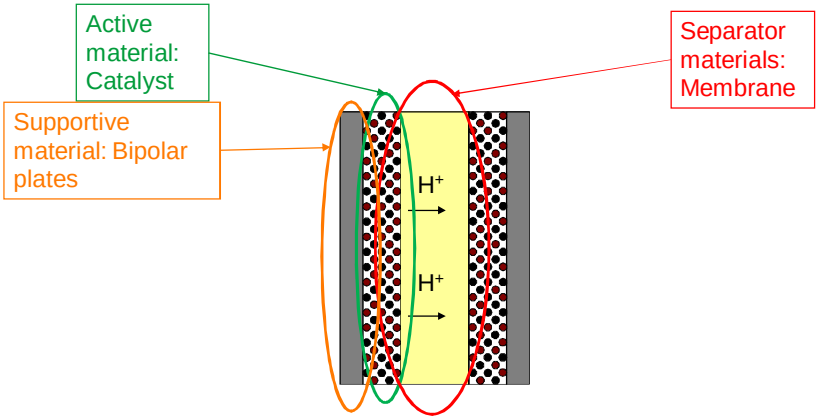
Total: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$

Different components



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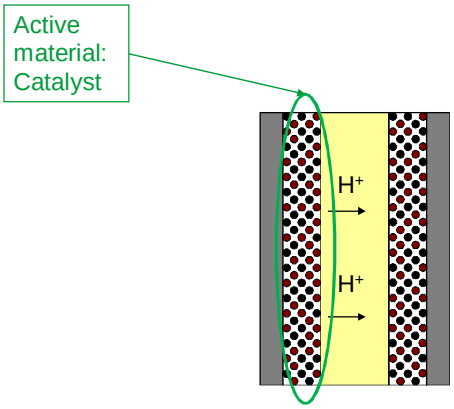
Degradation – Active Materials



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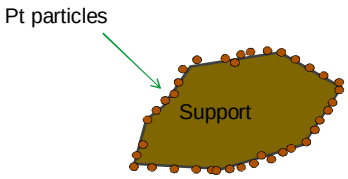
High activity catalyst

- High specific surface area
  - A lot of surface sites for the reaction to occur



  - Need for support material
    - very porous
    - high surface area
    - conductive (carbon)

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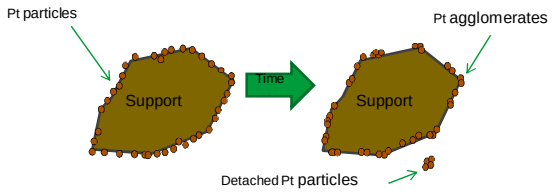
High activity catalyst

- High specific surface area
  - >strong driving force to form larger agglomerants



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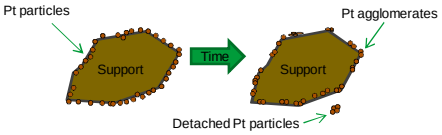
Nanoparticles

- High specific surface area
  - >strong driving force to form larger agglomerants



- Three mechanisms for agglomeration:
  - Ostwald ripening
    - Small particles dissolve in the ionomer phase and redeposit on surface of larger particles

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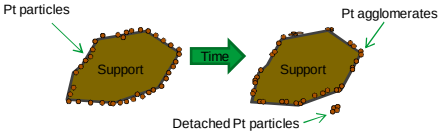
Nanoparticles

- High specific surface area
  - >strong driving force to form larger agglomerants



- Three mechanisms for agglomeration:
  - Ostwald ripening
  - Cluster-cluster collision
  - At the atomic scale minimizing clusters' Gibbs energy

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Nanoparticle agglomeration

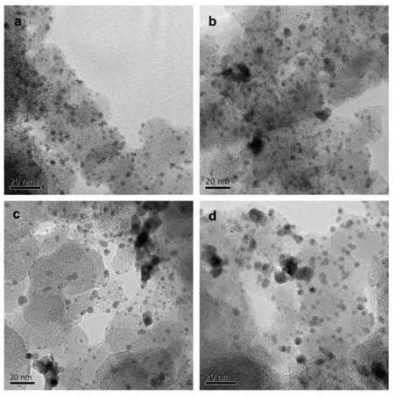

Fig. 6 – TEM images of the Pd/C at 0 h (a), 100 h (b), 300 h (c) and 500 h (d).

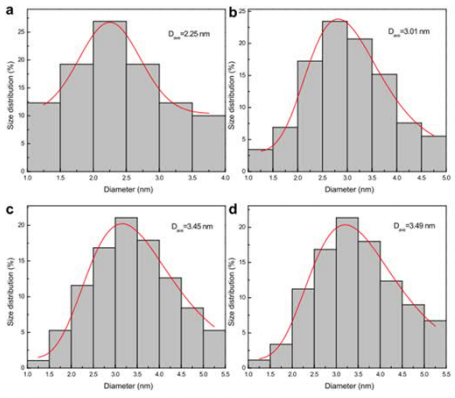

Fig. 7 – Histograms of Pd particle size distribution at 0 h (a), 100 h (b), 300 h (c) and 500 h (d).

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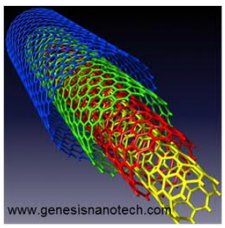
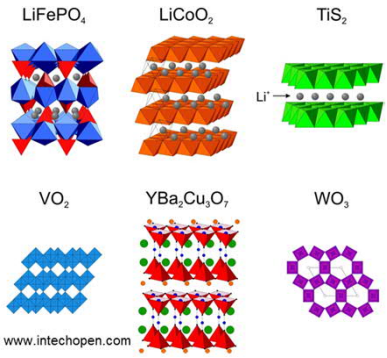
Y.S. Li, T.S. Zhao, International Journal of Hydrogen Energy, 37 (2012) 4413-4421.

3D materials

- Structures
  - Carbon nanotubes
  - Li-ion materials
  - Do they collaps?





Positive electrode materials for Li-ion batteris

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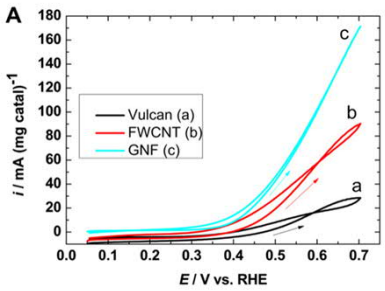
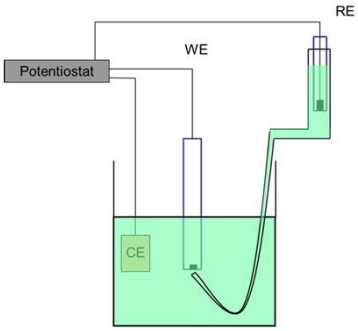
3D materials: activity





In electrochemical cell:
25 ºC
0.1 M HClO4 + 1 M MeOH

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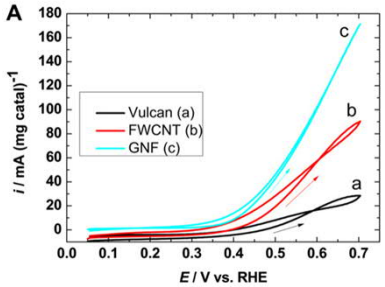
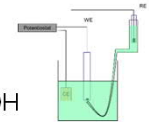
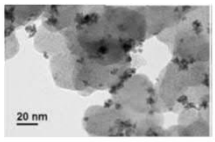
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

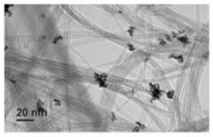
3D materials: activity



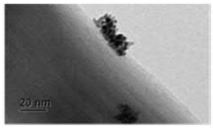




PtRu/Vulcan



PtRu/FWCNT



PtRu/GNF

In electrochemical cell:
25 ºC
0.1 M HClO4 + 1 M MeOH

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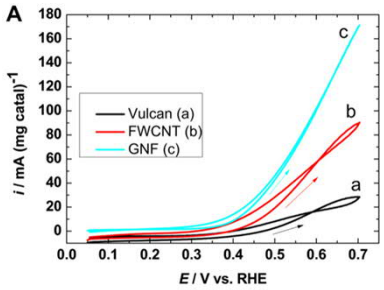
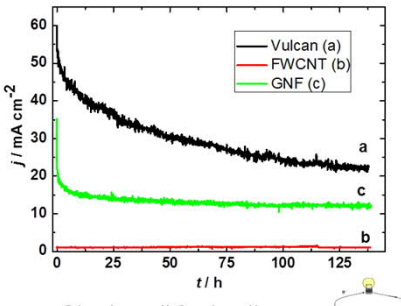
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

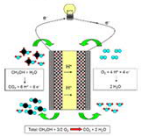
3D materials: durability



In electrochemical cell:
25 ºC
0.1 M HClO4 + 1 M MeOH



Single cell fuel cell:
70 ºC
1 M MeOH



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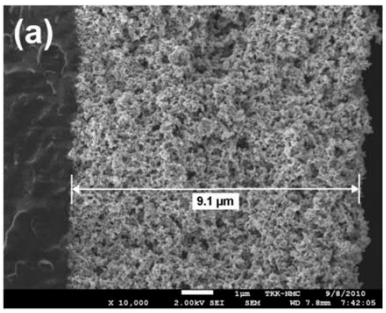
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

3D materials: Durability

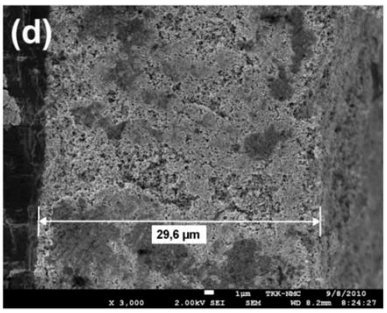
- PtRu/Vulcan anode

Membrane electrode assembly (MEA)

A M C



New



After 130 h

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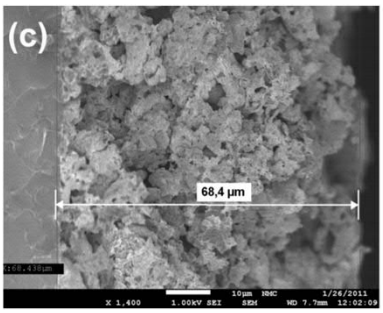
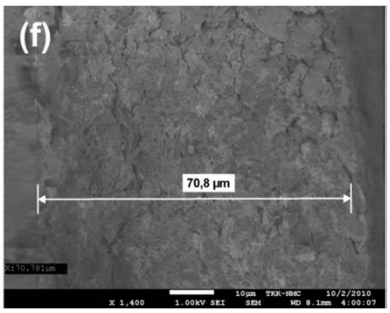
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

3D materials: Durability

- PtRu/FWCNT anode





New After 130 h

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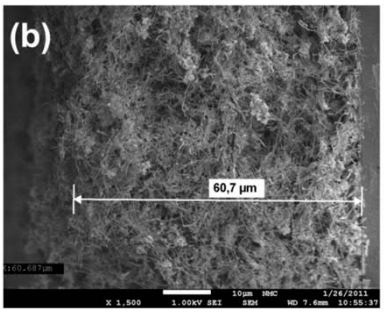
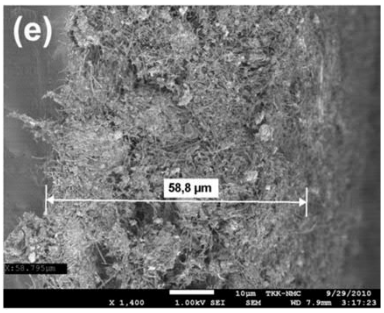
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

3D materials: Durability

- PtRu/GNF anode





New After 130 h

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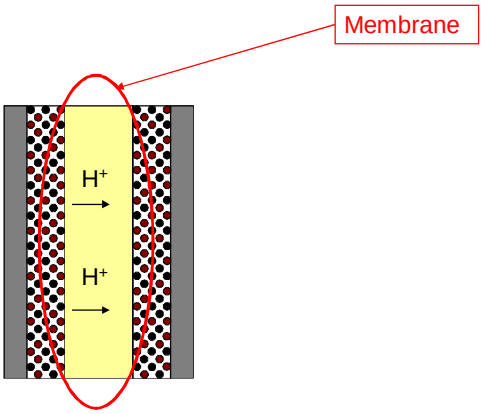
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

Degradation – Separator Materials



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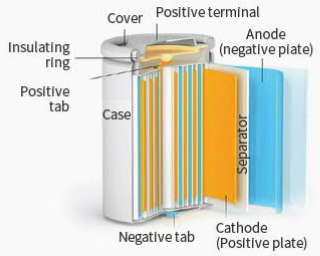
Separators

Separate the anode and cathode reactions

- Possible parasitic products formation



www.ftene.com

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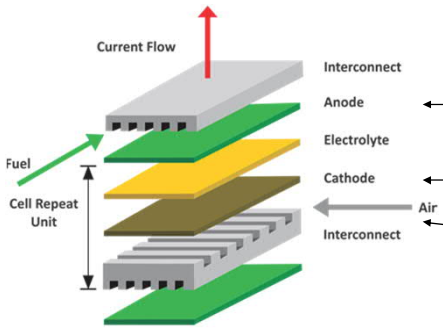
High temperature materials



Planar SOFC configuration

h2epower.net

Ceramic materials
Temperature dependent

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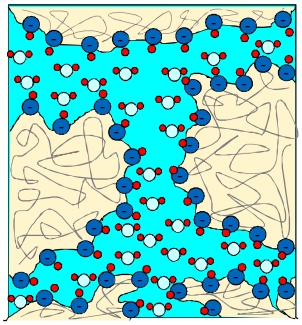
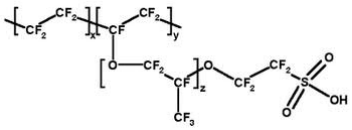
Nafion membrane

- Proton conductive membrane material
- Used in many electrochemical devices
  - Electrolysers
  - Fuel Cells
  - Flow batteries
- Required liquid water
  - (limits operating temperature)





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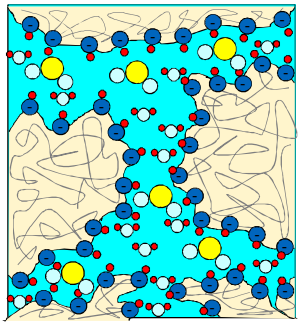
Nafion crossover

- Small, neutral molecules
  - Alcohols (DMFC)
  - SO_2 (SO_2 depolarised electrolyser)
- Prevention:
  - Different electrolyte material
  - Finding reactant that have charge (neg.) Formic acid
  - Protective layer to prevent molecules to enter the electrolyte



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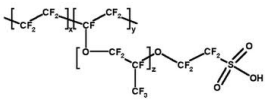
A. Santasalo-Aarnio et al. J. Solid State Electrochem (2016)
DOI: 10.1007/s10008-016-3169-8

Nafion durability



- Nafion has high chemical durability however, does not last well dry conditions

Case – Dry conditions (T.-C. Jao, Int. J. Hydr. Ene 37 (2012) 13623-13630.)

- Accelerated membrane test
- Step 1: The MEA was operated in OCV mode for 30 s under 100 % Humidy (R.H);
- Step 2: The MEA was operated in discharge mode at 0.6 V for 150 s under R.H. 100%;
- Step 3: The MEA was operated in discharge mode at 0.6 V for 150 s under R.H. 0% (bypass).

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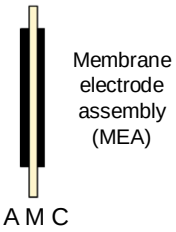
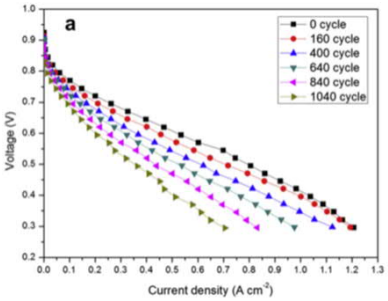
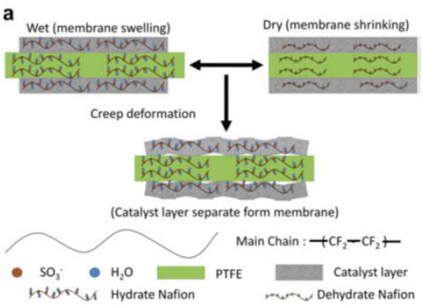
Nafion degradation with accelerated test







T.-C. Jao et. al. *Int. J. Hydr. Ene* 37 (2012) 13623-13630.

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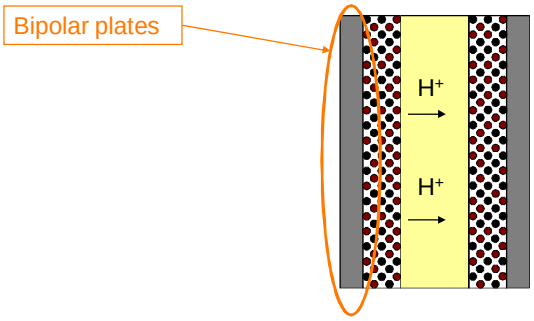
Degradation – Supportive Materials



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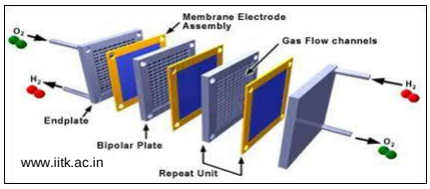
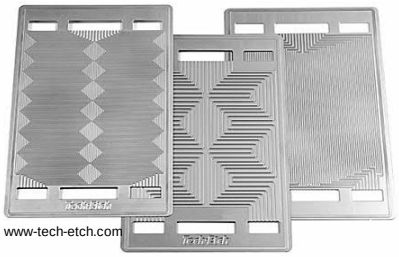
Corrosion: Bipolar plates

- For high voltage -> stack of cells in series
- Bipolar plates
  - Stainless steel
  - Carbon





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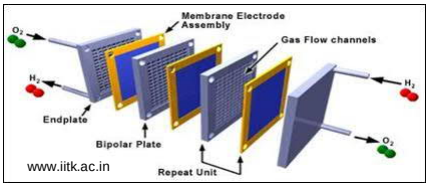
Degradation: Carbon

- Carbon used in
  - a support material for catalyst
  - Carbon cloth used for gas diffusion layer material in PEMFCs
  - Bipolar plates in multicell stacks (light)



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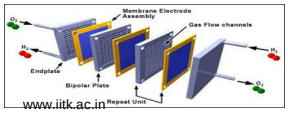

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- Carbon corrosion

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

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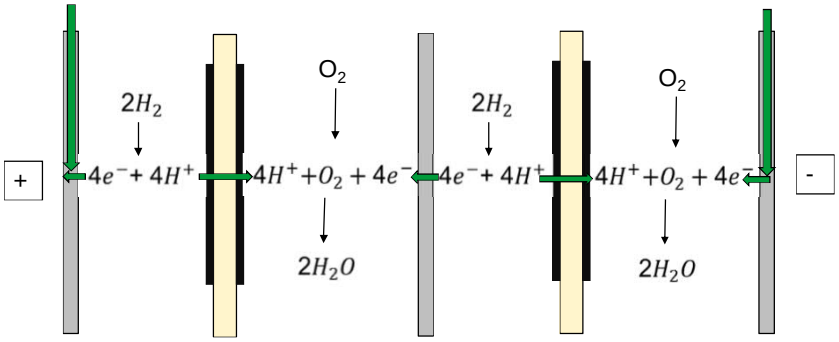
Case: PEM FC in a car (Diamler)



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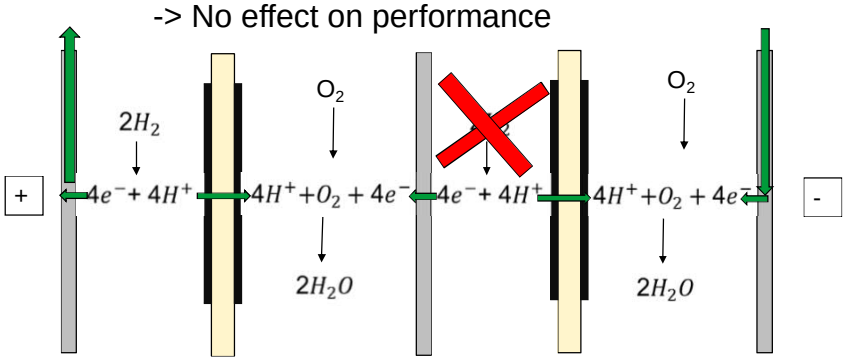
Case: PEM FC in a car (US)

H_2 loss in one cell in the stack
-> No effect on performance



What happend?

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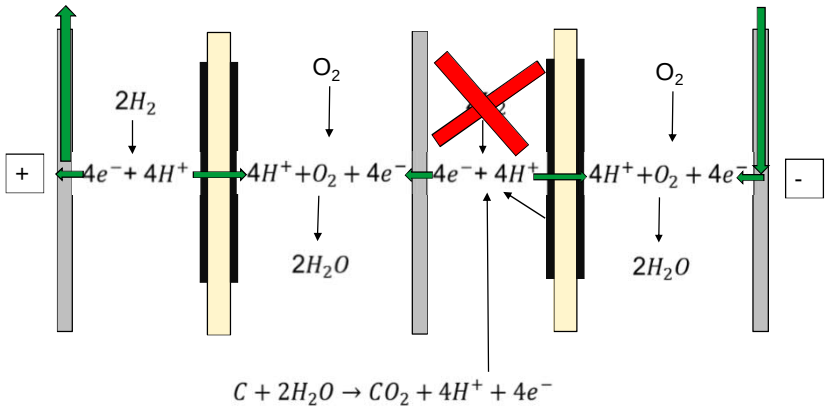
Case: PEM FC in a car (US)

H_2 loss in one cell in the stack



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In failure mode – competing reactions

Possible electrochemical reactions at PEMFC anode

Fuel Cell	$H_2 \rightarrow 2\,H^+ + 2\,e^-$	E^0= 0 V [1]
Carbon	$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$	E^0= 0.5 V [2]
Water splitting	$2\,H_2O \rightarrow 2\,H^+ + 2\,e^- + O_2$	E^0= 1.23V [1]

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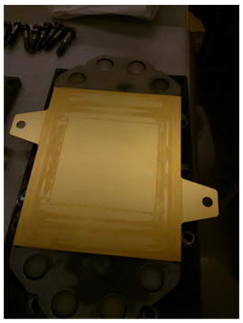
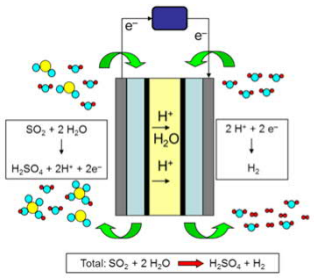
1) R.C. Weast, CRC handbook, 56th Edition (1975)
2) C.A. Reiser *et al*. *Electrochemical and Solid-State Letters*, **8** (2005) A273-A276

SO_2 depolarized electrolyser (SDE)

- Stainless steel 904L plates with 100 nm Au coating
  - Works for anode and cathode plate + catalyst





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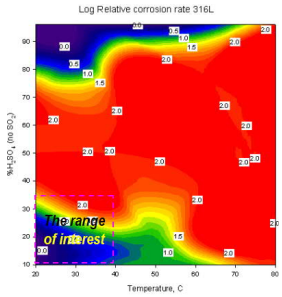
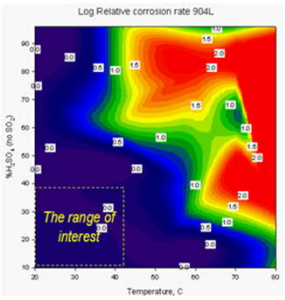
Corrosion: bipolar plates

Corrosion rate (log mm/year)



Stainless steel 316L
Marine grade



Stainless steel 904L
NiCrMoCu 25/20/5/1

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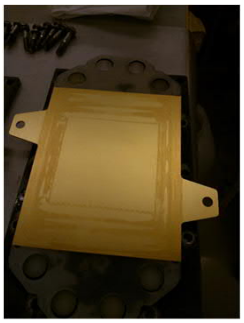
A. Santasalo-Aarnio et al. J. Power Sources 306 (2016)1-7.

Case: corrosion in SDE

- Stainless steel 904L plates with 100 nm Au coating
- Catholyte 15 wt% H_2SO_4
- Anolyte: 15 wt% H_2SO_4
  Saturated SO_2
- Stack of 5 cells
- 25 ºC
- Constant current experiments 11 A



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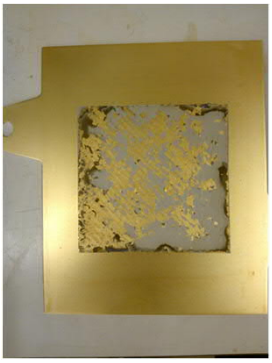

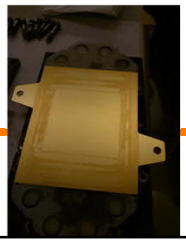

What happend?

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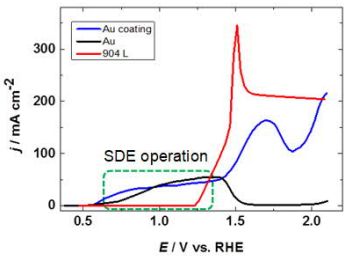
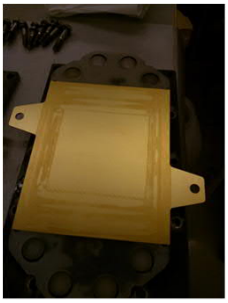
Case: corrosion in SDE

- Stainless steel 904L plates with 100 nm Au coating





- Plate at high potential, dissolution of steel under the coating

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Reflection

1. What was most interesting today?
2. I would have wanted to hear more on?

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Next workshop IV

Next workshop IV

- What are the most important degradation mechanisms in your application?

  -> Poster's with that

- Theory: the challenges of material substitution – What need to be taken into account?

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Flip report III:

1) "The European Critical Raw Materials review"
Memo by European Union, ALL STUDENTS
MyCoursese – Materials – Material Development

2) Paper clip: "Material challenges"
Preferable in your application (if not found any on course topic)
(any country, any language)

3) Journal Paper: "Durability issues" in your application
(Each student should have a different paper -> poster)

You can coordinate that you would not have same journal paper:
For instance agree who will have some on
- Active material (Anode + Cathode)
- Electrolyte
- Support material …

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Flip reports – peer review

- Student number to your task

- Select one flip that is from other topic than your own
- Read and evaluate the report (15 min.)
- Write at least 2 sentence of feedback
  - What was good/interesting or/and what could be improved
- Grade
  - 3 p. Excellent work
  - 2 p. Good work
  - 1 p. Some parts missing/ Unclear text
  - 0 p. No submission

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