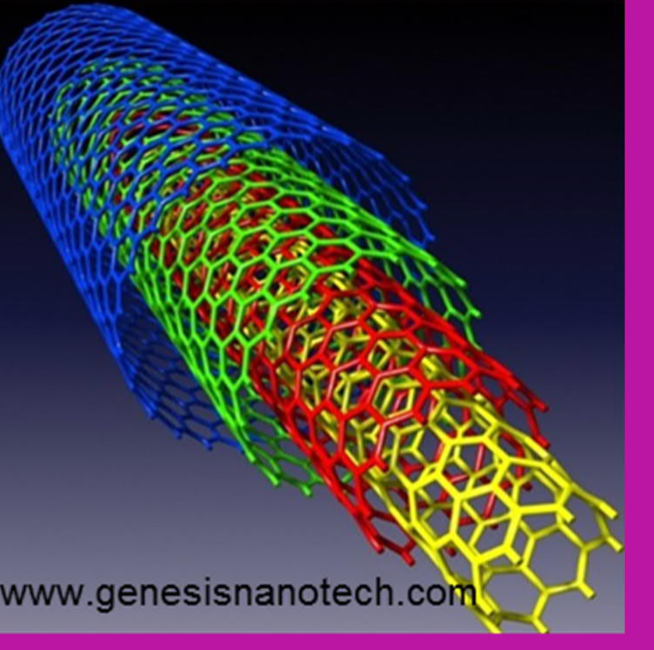
# Module C1: Durability - Nanostructures

## AAE-E3120 Circular Economy for Energy Storage




Prof. Annukka Santasalo-Aarnio

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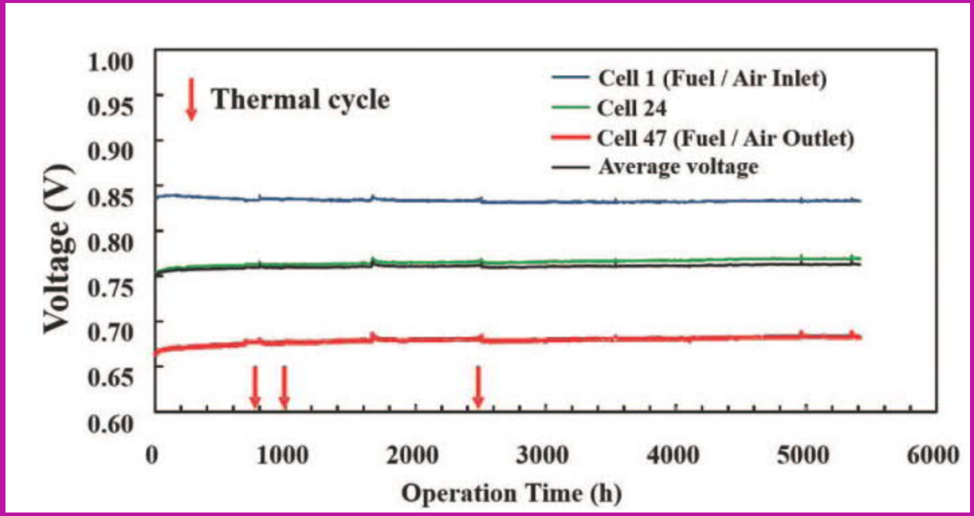
# Learning outcomes

- **Recognize the material choice effect to degradation mechanisms of the system**
  - Degradation mechanism in
  - Active materials (nanomaterials)

- **Develop new design for recycling approach for energy storage application and justify with scientific argumentation**
  - High durability (how to ensure with material selection?)

# Definition of Durability




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

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# Durability ?

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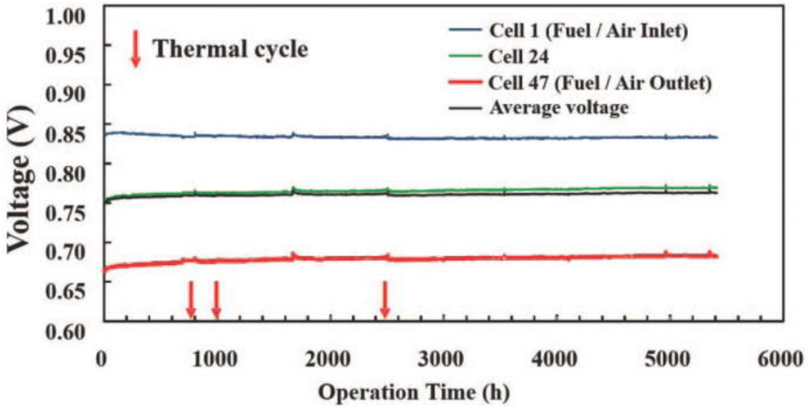
How to define durability?

How often you are willing to

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

# Durability ?

## Close to market applications

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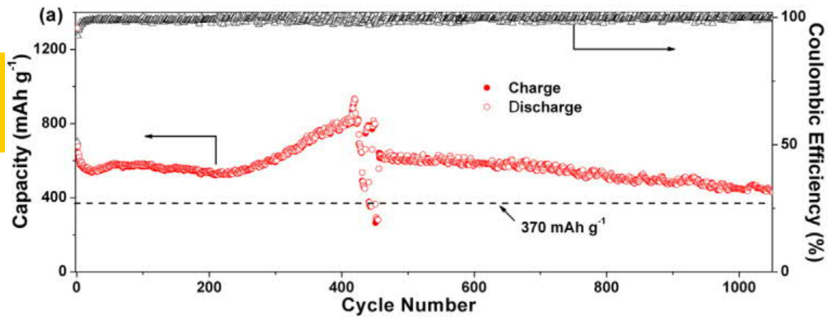
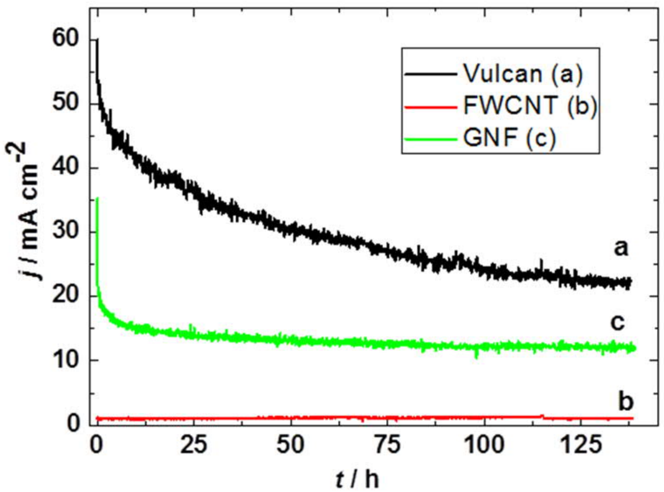


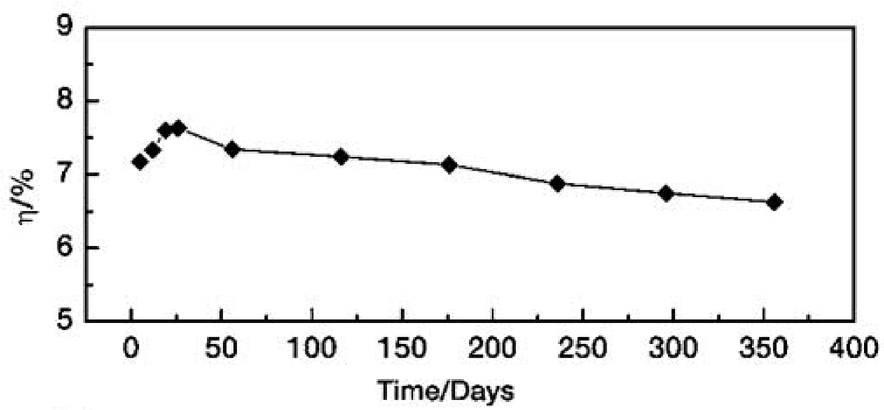

**Li-ion batteries**
X. Zhang et al. / Journal of Power Sources 268 (2014) 365-371

# 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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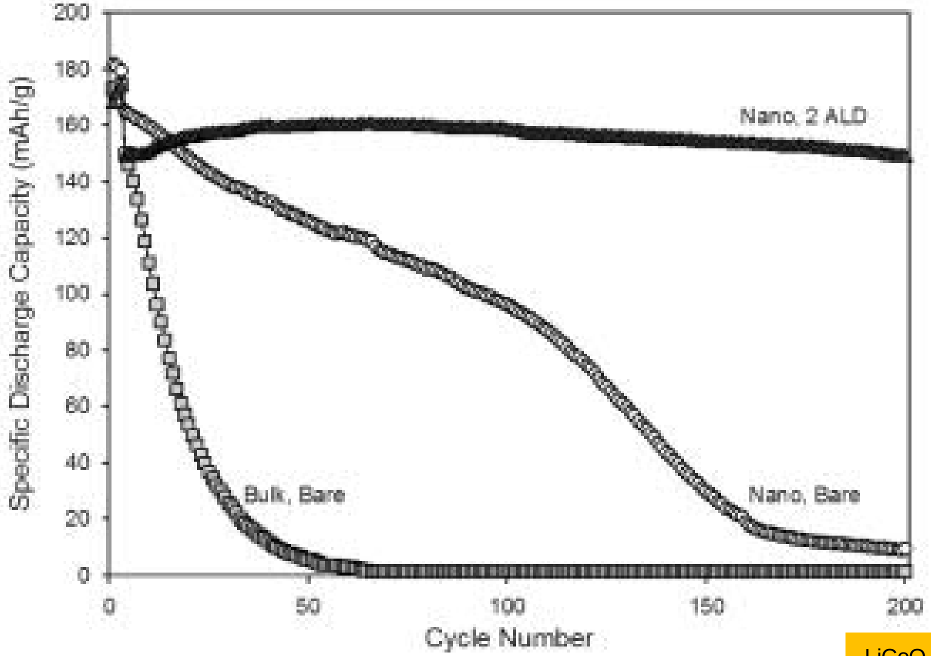
# Material degradation

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

What is presented as reference data?




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.

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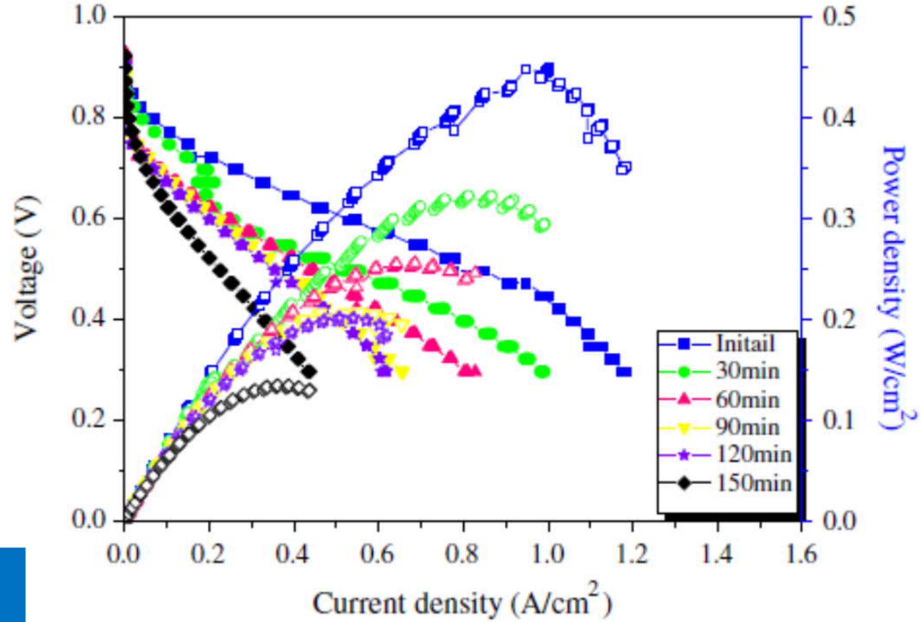
# How to measure durability?

## Accelerated durability test

- Speed up the degradation
- Unrealistic conditions?

Case: PEM FuelCell

At start-stop cycles a cell can
Jump to 1.5 V (for seconds)

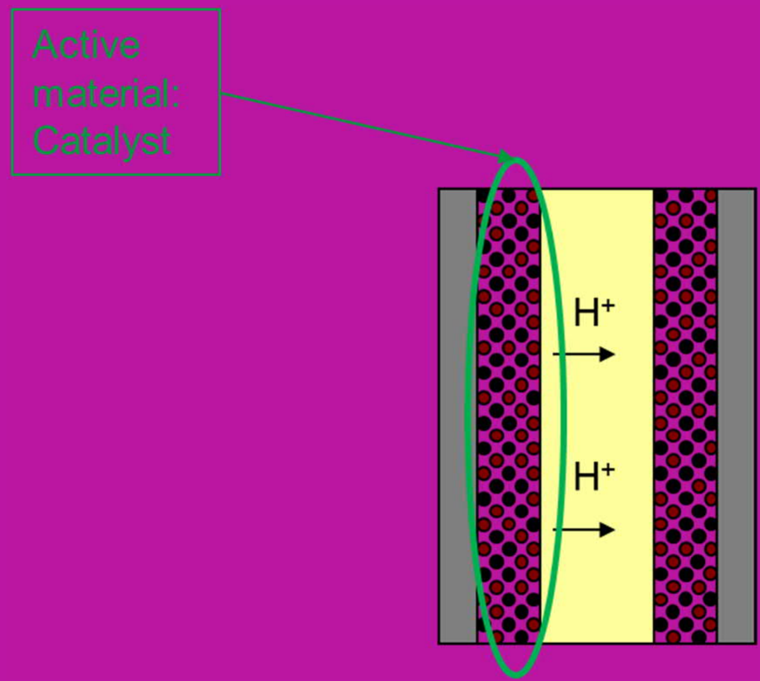



G.-B. Jung et al. Applied Energy 100 (2012) 81-86.

**Lecture Journal**

What do you think, are these tests useful? What else could we do?

# Degradation mechanisms of nanoparticles

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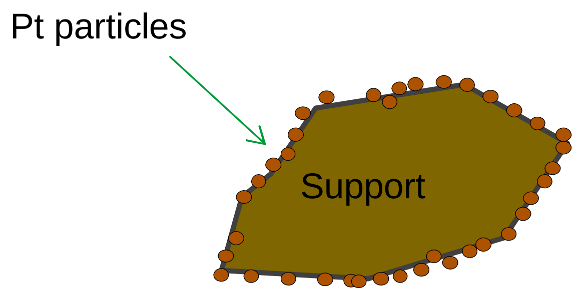
# Durability – High activity catalyst

- 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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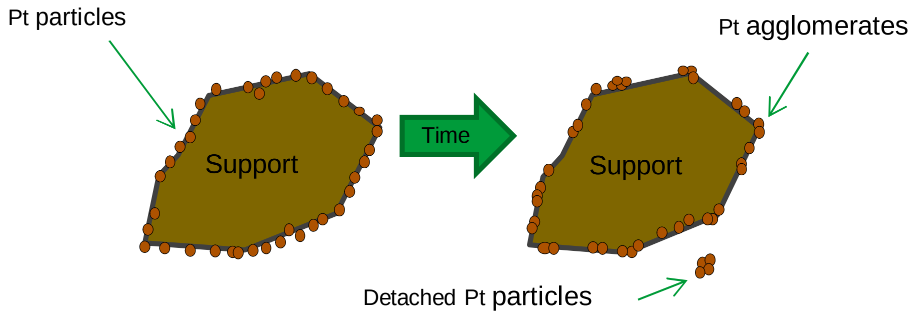
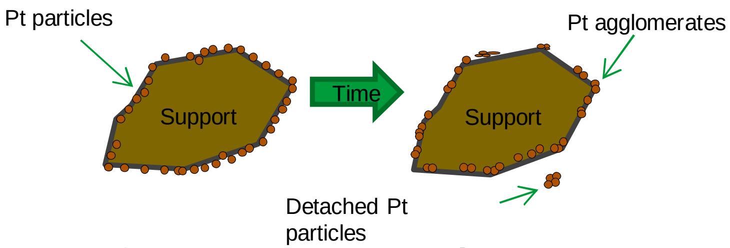
# Durability – High activity catalyst

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



# Durability – 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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# Durability – Nanoparticles

- High specific surface area
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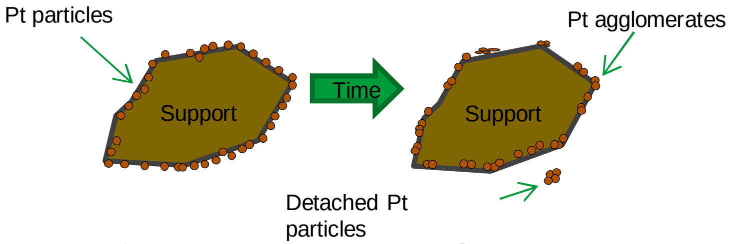


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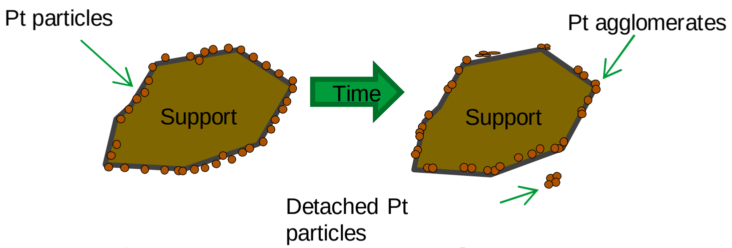


- Three mechanisms for agglomeration:
  - Ostwald ripening
  - Cluster-cluster collision
  - At the atomic scale minimizing clusters' Gibbs energy

# Nanoparticle Agglomeration

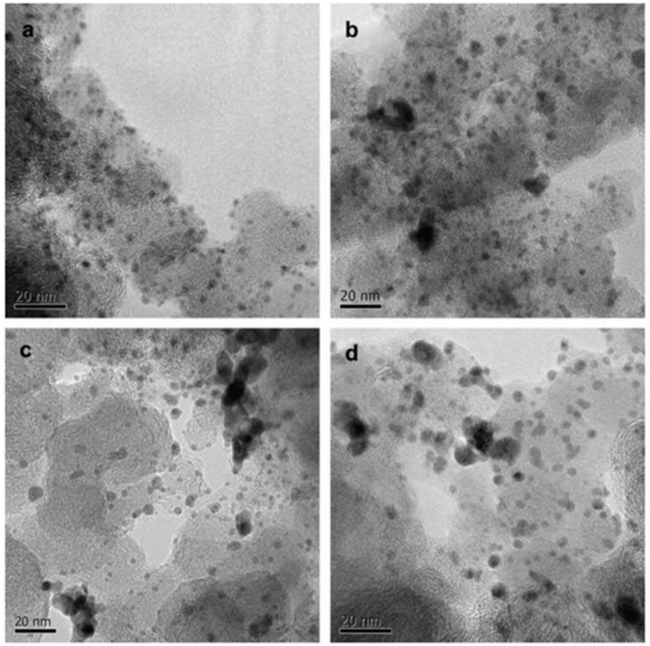


Fig. 6 – TEM images of the Pd/C at 0 h (a), 100 h (b), 300 h (c) and 500 h (d).

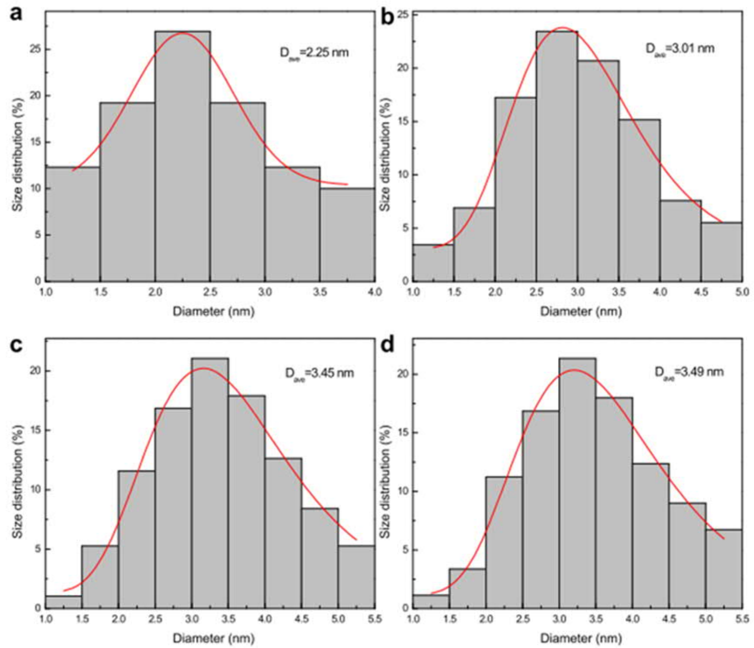


Fig. 7 – Histograms of Pd particle size distribution at 0 h (a), 100 h (b), 300 h (c) and 500 h (d).

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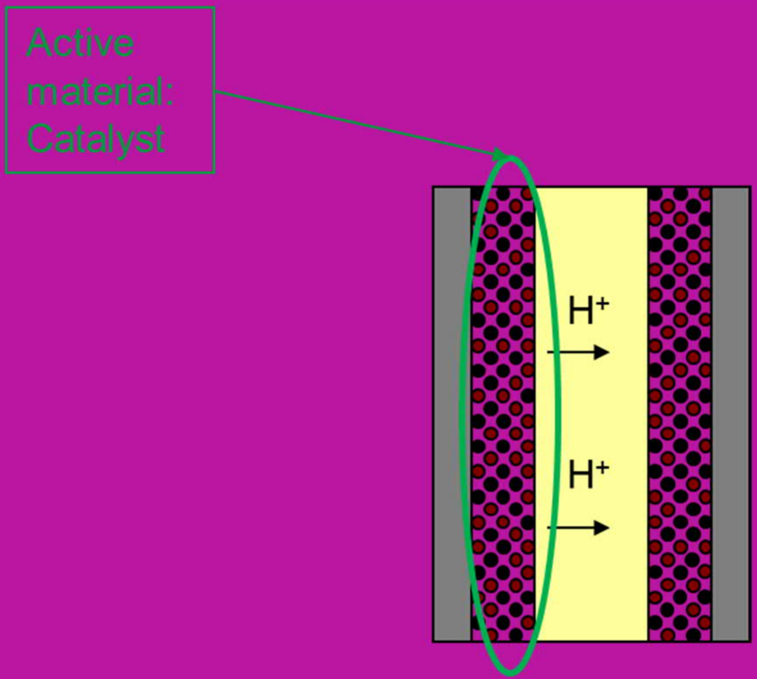
Y.S. Li, T.S. Zhao, International Journal of Hydrogen Energy, 37 (2012) 4413-4421.

# Degradation challenges on 3D materials

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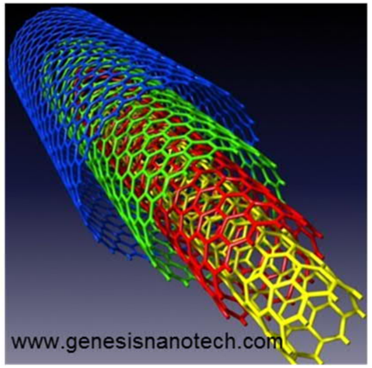
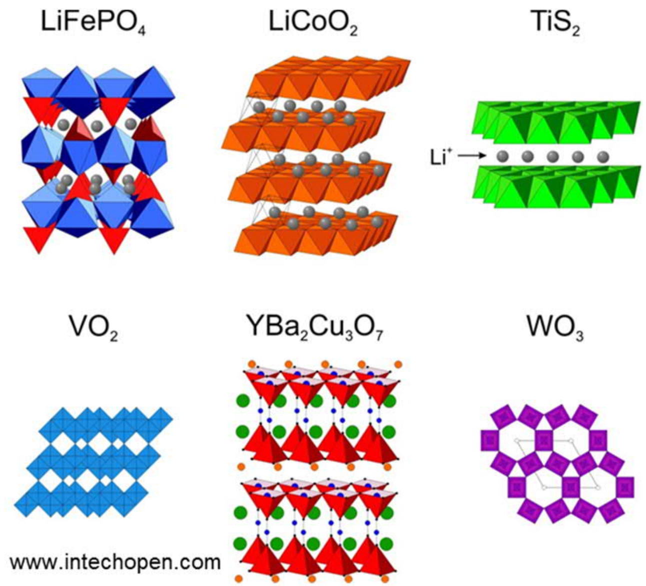
# 3D Materials

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




Positive electrode materials for Li-ion batteris

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Reflect, how do we know/ensure the 3D material durability?

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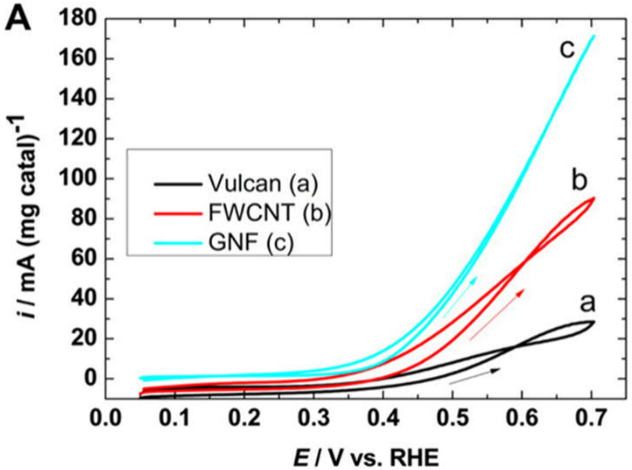
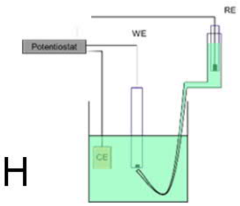
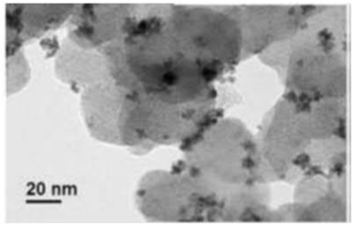
# 3D: Materials

# Durability and Activity

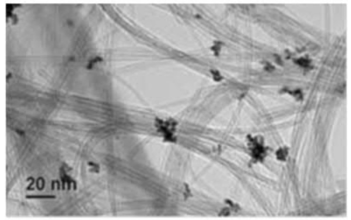



In electrochemical cell:
25 ºC
0.1 M HClO4 + 1 M MeOH

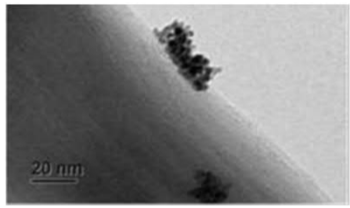



PtRu/Vulcan



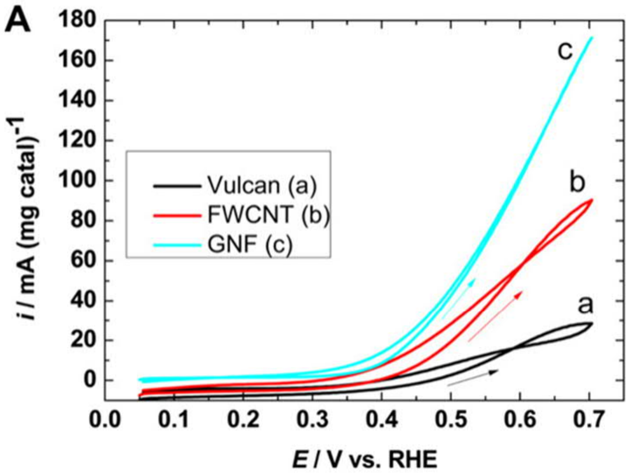

PtRu/FWCNT

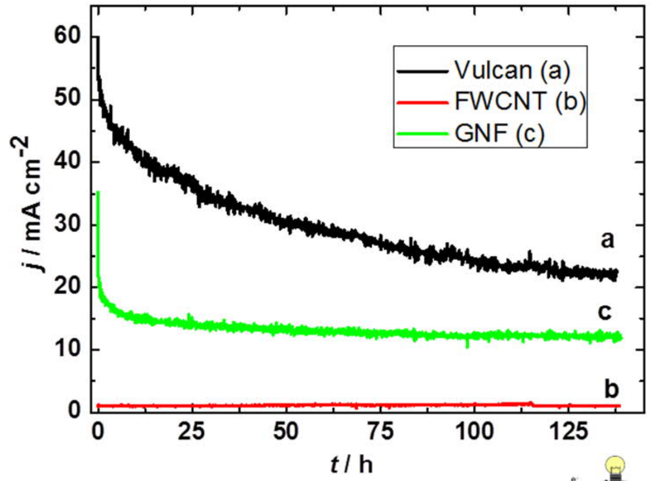



PtRu/GNF

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

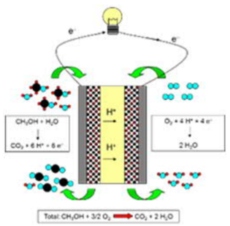
# 3D: Materials
# Durability and Activity




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

Single cell fuel cell:
70 ºC
1 M MeOH



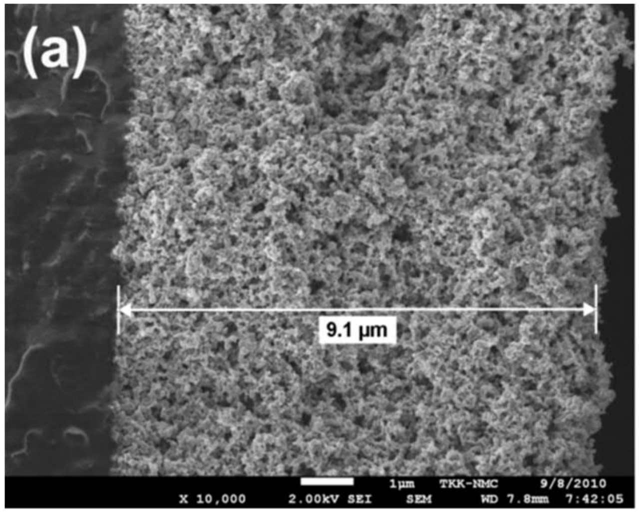


A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

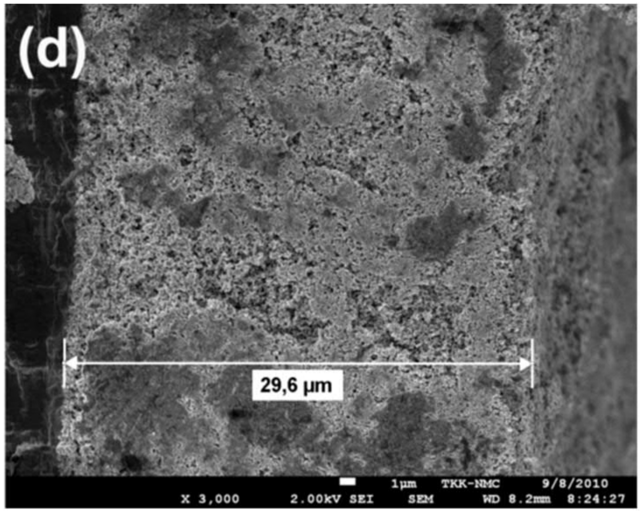
# 3D: Materials

# Durability and Activity

- PtRu/Vulcan anode


New




After 130 h

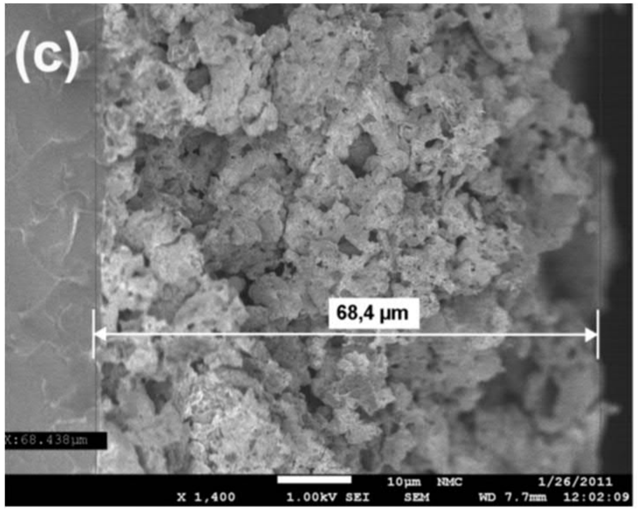


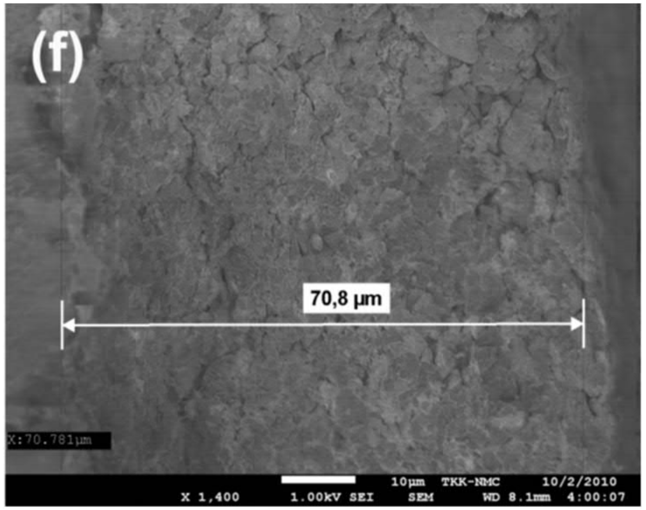
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

# 3D: Materials

# Durability and Activity

- PtRu/FWCNT anode




New

After 130 h



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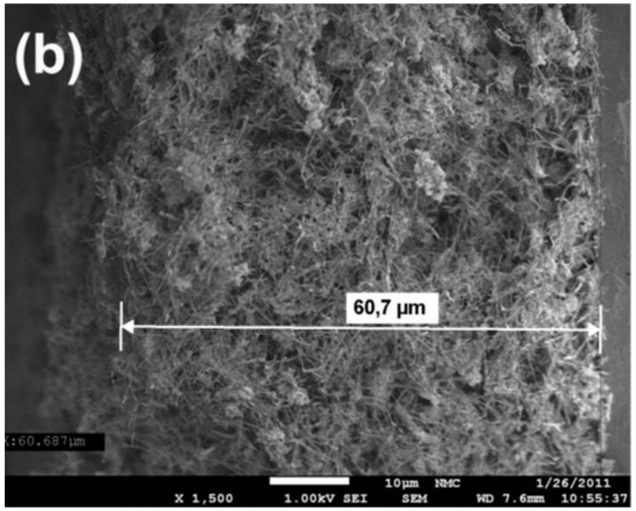
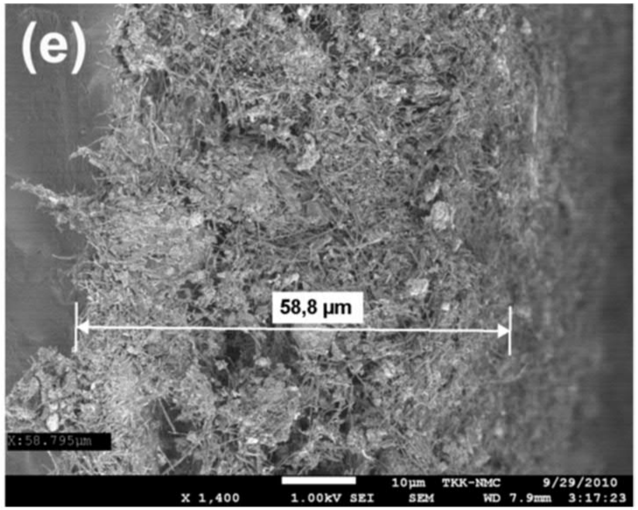
# 3D: Materials

# Durability and Activity

- PtRu/GNF anode




New




After 130 h

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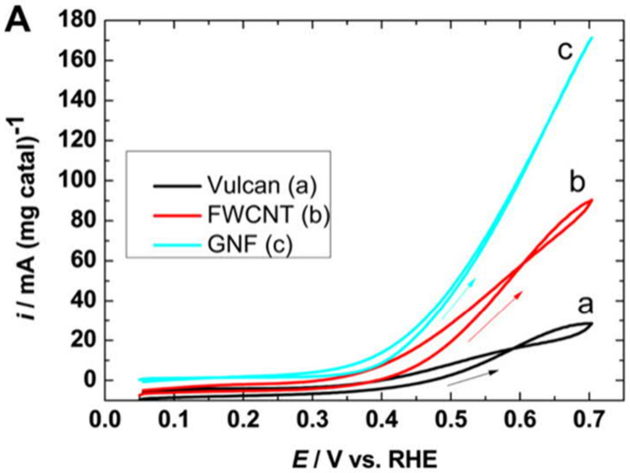
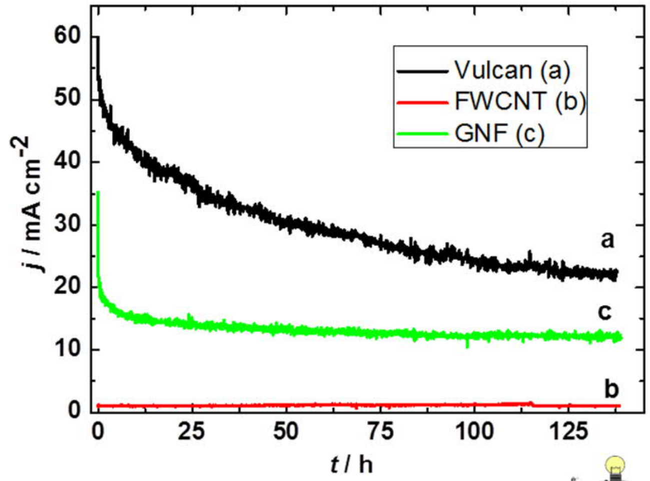
# 3D: Materials
# Durability and Activity

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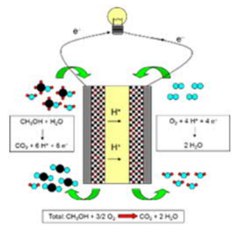

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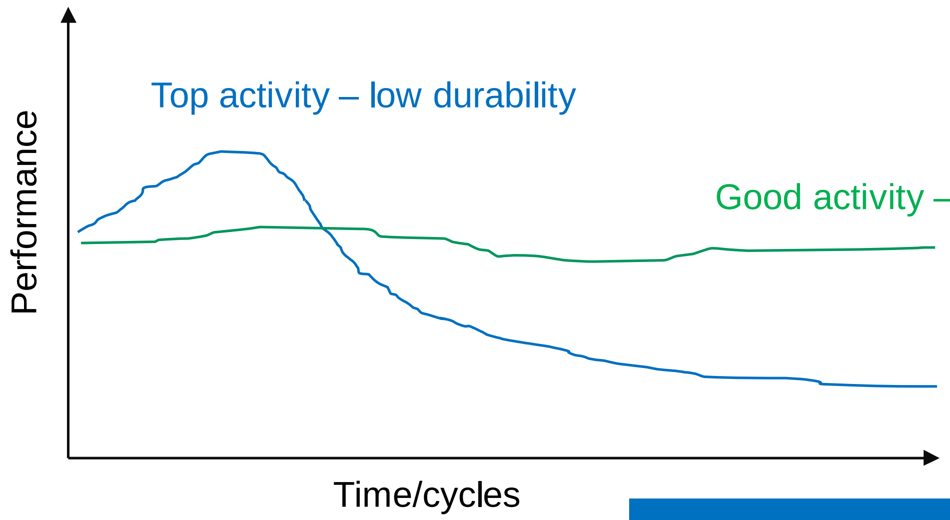
# What is valued in active material performance?




Performance

Durability

Recyclability –
Not yet here…

**Lecture Journal**

Reflect, as a consumer – which application would you choose?

# Take a home message

**At science, there are large interest to produce exotic active materials for these solutions. But,** ***thermodynamics*** **is against that – sometimes, robust systems are most efficient (as they are stable).**

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