Iron carbide nanoparticles encased in graphitic layers as oxygen reduction catalysts for fuel cells

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Outline

- Renewable energy in Denmark
- NPMCs – a brief yet long history
- A new type of active sites?
  - High pressure pyrolysis of volatile precursors
  - Hollow spherical structures of graphitic encapsulation
  - Iron Moieties – Fe₃C nanoparticles
  - Activity and Active Site Exploration
  - LT- and HT-PEMFC tests
- Carbon encapsulated Pt alloys
  - An Approach to Stabilizing Pt and its Alloys?
- Acknowledgement
Renewable Energy in Denmark:

2020 2030 2035 2050
Half of the traditional coal is phased out from Danish power plants. The electricity and heat supply covered by renewable energy. All energy supply – electricity, heat, industry and transport – is covered by renewable energy.

Windmills - an intermittent power source of 8760 hours of 2015
- 1460 hours West Denmark produces more than 100% power consumed
- 65 hours with negative prices (to turn off the wind turbines)

Wind Power Production and Net Exports, Western Denmark 2002

- Fluctuating with no warning in shorter or longer terms
- Fluctuating span over 50% of the primary power capacity
- A giga watt level of grid levelling

Updated 2016.01.15
The Hydrogen Chain
- a Danish strategy

Electrolyser (20 MPa CGH₂)

Windmill

Electrolysers & fuel cells

Truck to deliver (20 MPa CGH₂)

H₂ Station (stored 40 MPa)

FC vehicles (CGH₂ 35MPa)

The Hydrogen Chain

Conclusions:
- Significant reduction of PGM or non-precious metal catalyst

Based on current technology, planned for commercialization in the 2016 time frame:
- $280/kW for 20,000 units/year volume

Table 2. Key Assumptions of Cost Analyses and Resulting Cost

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
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<tr>
<td>Stack power</td>
<td>kW</td>
<td>90</td>
<td>90</td>
<td>88</td>
<td>88</td>
<td>89</td>
<td>88</td>
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<tr>
<td>System power</td>
<td>kW</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
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<tr>
<td>Cell power density</td>
<td>kW/ft²</td>
<td>563</td>
<td>715</td>
<td>833</td>
<td>833</td>
<td>1,110</td>
<td>984</td>
<td>692</td>
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<tr>
<td>Peak stack temperature</td>
<td>°C</td>
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<td>80.00</td>
<td>80.00</td>
<td>90.00</td>
<td>90.00</td>
<td>87.00</td>
<td>97.00</td>
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<tr>
<td>PGM loading</td>
<td>mg/cm²</td>
<td>0.35</td>
<td>0.25</td>
<td>0.15</td>
<td>0.15</td>
<td>0.19</td>
<td>0.20</td>
<td>0.15</td>
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<tr>
<td>PGM total content</td>
<td>g/kW</td>
<td>0.6</td>
<td>0.35</td>
<td>0.18</td>
<td>0.18</td>
<td>0.17</td>
<td>0.20</td>
<td>0.23</td>
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<tr>
<td>PGM total content</td>
<td>g/kW</td>
<td>0.68</td>
<td>0.39</td>
<td>0.20</td>
<td>0.20</td>
<td>0.19</td>
<td>0.22</td>
<td>0.25</td>
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<tr>
<td>Pt cost</td>
<td>$/troy</td>
<td>1.100</td>
<td>1.100</td>
<td>1.100</td>
<td>1.100</td>
<td>1.100</td>
<td>1.100</td>
<td>1.500</td>
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<tr>
<td>Stack cost</td>
<td>$/kW</td>
<td>50</td>
<td>54</td>
<td>27</td>
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<td>24</td>
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<td>37</td>
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<tr>
<td>Balance of plant cost</td>
<td>$/kW</td>
<td>42</td>
<td>57</td>
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<td>25</td>
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<td>26</td>
<td>27</td>
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<td>Sys. Asy. and Testing</td>
<td>$/kW</td>
<td>2.2</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>System cost</td>
<td>$/kW</td>
<td>94</td>
<td>73</td>
<td>61</td>
<td>51</td>
<td>49</td>
<td>47</td>
<td>55</td>
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</tbody>
</table>
M-Nₓ/C catalysts
- a brief yet long history

The heme group of cytochromes exhibits electronic conductivity via inter-conversion between Fe²⁺ and Fe³⁺
- a capability of performing oxidation and reduction within the cell membranes

![Porphyrin substituted porphines](image1)

Cytochrome C

M₂⁺ - MgII, CoII, FeII

1964, R. Jasinski
Nature, March 12, 1964
Activity towards ORR in alkaline

- Metals as active sites for ORR
  - Co & Fe the best
- Ring substitute groups

Separated metal ion, nitrogen, and carbon precursors
Yeager et al., J. Appl. Electrochem., 1989

Heat-treatment of metal macrocycles
- 500–900 °C in inert gas
Dedelet et al., 2002

A long way to achieve the status

Conclusive remarks of earlier work
- Metal macrocycle complexes - expensive
- Moderate ORR activity
- Poor stability
- H₂O₂ formation and attack
- Metal leaching out of macrocyclic complexes
Synthesis of “Modern” NPMCs
- Pyrolysis of separate M-, N- and C- precursors

Metal sources

<table>
<thead>
<tr>
<th>Metal sources</th>
<th>Nitrogen sources</th>
<th>Carbon sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcycle: Fe, FeC, FeP, FePc, FeT, FeCIP, FeCIP, FeCIP, FeCIP</td>
<td>Organic: Ethylenediamine, 1,10-Phenanthroline, Nitroaniline, Ammonia, HCN, Cyanamide</td>
<td>Ketjen black EC-600JD (Akzo Nobel)</td>
</tr>
<tr>
<td>Inorganic salts: Fe, Mn, Co</td>
<td>Inorganic salts: Fe, Mn, Co</td>
<td>Acetylene black (Chevron)</td>
</tr>
<tr>
<td>Organometallic complex: Ferrocene, CoPc, CoPc, CoPc, CoPc</td>
<td>Organopolymer: Polyvinylpyridine</td>
<td>Vulcan XC-72R (Cabot)</td>
</tr>
<tr>
<td>Microcycle: Co, Co, Co, Co, Co</td>
<td>Inorganic salts: Co, Co, Co, Co, Co</td>
<td>Black Pearls 2000 (Cabot)</td>
</tr>
<tr>
<td>Inorganic salts: Co, Co, Co, Co, Co</td>
<td>Organic: Ammonium iron sulfate</td>
<td>…….</td>
</tr>
</tbody>
</table>

Metal precursor

Nitrogen precursor

Carbon support

ORR activities of M–Nx/C catalyst
- strongly dependent on precursors
- heat-treatment temperatures
- carbon support morphologies
- synthetic approaches

One significant approach – by Dodelet et al. Quebec, Ca. Science 2009

NH₃ as N precursor in atmosphere
- super activity
- however poor stability

Hypothesis I:
• Active sites are of type Me-Nₓ/C species
• Metals play a central role in catalysis

Using polypyrrrole to entrap Co      - to mimic cobalt porphyrins to develop Co-N sites

Debates of Catalytic active sites

Active sites:  
N-doped carbon without the participate of metal ion

Hypothesis II:  
- Active sites are of type of N_x/C species  
- Metals catalyze the formation of C-N functionalities (pyridinic/quaternary nitrogen)

One thing seems clear:  
Nitrogen is involved in the central active sites

What is interesting:  
We find another type of NPMCs where NITROGEN plays a trivial role...

Synthesis of NPMCs

**Variations**
- each of three precursors
- ratios of precursors
- pre-mixing techniques

**Precursors**
- A metal source: metal salts
- A nitrogen source: NH₃ or cyanamide or heterocyclic compounds/polymers
- A carbon source: microporous carbon blacks, CNTs, etc.

**Pyrolysis at elevated temperatures under ambient pressure**
- The heat-treatment temperature
- Duration & atmospheres
- Subsequent heat-treatments

**Challenging issues**
- Nature of active sites
  - Nitrogen involved sites, coordinated with metal atoms?
- Enhanced activity
  - and long term durability
- Electrode engineering
  - Thick catalyst layers:
    - Volumetric activity / high catalyst loading
    - Conductivity; Ionomer; Porosity

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**High pressure pyrolysis**
An approach to higher active site density?

**Swagelok like reactor**
- Gold lining coating
- Quartz tubing
- Up to 900°C
- > 200 bar
  - tailored by volume/charge
  - checked by mass change
  - solid yield
  - all in an inert atmosphere

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Critical point
274°C, 217 atm
**High pressure pyrolysis**

- **Limited decomposition/evaporation** due to pressure buildup
- **Close system**
  - no removal of gas products
  - little morphology change of condensed phase
  - low porosity products
  - no carbon substrate added
  - volatile small molecule precursors

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**A new type of NPMC?**

- Hollow spheres of curved CNTs

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*Fe₃C/C-700*  
Little surface nitrogen!
Tailoring pressures
- amount of precursors
- tightening reactors

Morphologies
- spheres
- loose powders

Graphene wrapped particles
Favored at lower pressures
Favored at higher pressures

Nanotube wrapped particles

The iron moieties
- Nanoparticles
  ca. 10 nm
- Iron carbides

The iron moieties
- Nanoparticles
  ca. 10 nm
- Iron carbides
Iron moieties survived the acid leaching in 0.5M H$_2$SO$_4$/80°C/8h.

The extraordinary stability in acid media of the Fe$_3$C nanoparticles originates from the isolation by the carbon layers - but with no barrier effect on activity!

Further evidence of wrapping

Little ferrous functionalities On surface

Little surface site complexing with thiocyanate SCN$^-$

20% Pt/C - in 0.1M HClO$_4$ - + 5mM SCN$^-$

Fe$_3$/C-700 - in 0.1M HClO$_4$ - + 5mM SCN$^-$

5mM NaSCN Blank
Electrochemical activity towards ORR

- Excellent ORR activity, stability, nearly four-electron pathway in both alkaline and acid solutions.

High pressure pyrolysis
- at varied temperatures
- Spheres changed little in size
- N functionalities above 600 °C
High pressure pyrolysis
- at varied temperatures

Transition from 630 to 800 °C
- Varied N contents from 9 – 0.5 at%
- Significant formation of Fe₃C
- Remaining ORR activity

Iron phases identified
◆ α-Fe
◆ γ-Fe
◆ Ferrocene
◆ Fe₂O₃
◆ Fe₃N/C (LS)
◆ Fe₃C

57Fe-Mössbauer spectra

Phase composition varied
◆ Fe₃C content peaked
◆ Metallic phases steadily increased
◆ Fe-N coordination steadily decreased

Pyrolyzing at 700°C for 75 min
Correlation of electrochemical activity with iron containing components

- Good correlation with Fe-N phase - in a narrow range and with a saturation effect
- Good correlation with Fe$_3$C - through the wide range studied

**Active site exploration**

- Structure dependence
- Ball-milling and acid leaching
  - Fe$_3$C
    - isolated by carbon layers
    - super stability in acidic media
    - contributing to ORR activity
  - C-wrapped Fe$_3$C structure
    - synergies of Fe$_3$C and C
Summary

Hollow microspheres
- Uniform core Fe₃C nanoparticles
- Wrapping layers of graphene/CNTs
- Little surface functionalities of N/Fe

Synergetic mechanism
- Graphitic layers stabilized Fe₃C particles against acid leaching – chemical stability without depriving of catalytic activity
- Graphitic layers activated by wrapped particles

Nitrogen functionalities
- present in low temperature samples?

Preliminary fuel cell test
- Nafion cells at 80 °C
- PBI cells 120-180 °C
- Promising durability

- Nafion cell test at 80 °C
- Humidified H₂-O₂
- 0 – 2 - 7.7 – 26 – 50 hours
- Catalyst loading 3.95 mg cm⁻²

- H₃PO₄ doped PBI membrane
- Dry H₂-air operation
- Ambient pressure
- Fe₃C/C loading 3.9 mg cm⁻²

Chenitz et al.
Summary

- Prohibitive cost of PGM catalysts
- Significant progress on NPMC
  - Synthesis
  - Active site debate
  - Density of active sites – activity vs. stability
- High pressure pyrolysis
  - Volatile precursors
  - Simultaneous formation of metal moities and graphene layers
  - Synergy mechanism of encapsulated catalysts?
  - Separation of activity and stability?
  - An approach to stabilizing Pt alloys?

**Carbon encapsulated Pt alloys?**

- Uniform PtFe nanoparticles 10-20 nm buried in carbon
- FeN_x sites by N-1s and Fe-2p XPS (ca. 2.9 at% N and 0.2 at%Fe) which are catalytically active

<table>
<thead>
<tr>
<th>wt%</th>
<th>Fe</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS</td>
<td>6.76</td>
<td>8.13</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>7.14</td>
<td>8.92</td>
</tr>
</tbody>
</table>

\[
\text{PtFe}_{2.4} = \text{PtFe} + \text{FeN}_x + \text{Fe}_3\text{C} + \text{Fe}?
\]
Carbon encapsulated Pt

- XRD: PtFe alloy phase
- Pt-4f XPS:
  - At least partly buried
- N\textsubscript{2}-CV:
  - no H ad-/desorption peaks
- CO stripping
  - 10\% Pt surface area of JM-Pt/C
  - lower CO stripping potential
- Aqua Regia-ICP MS
  - more than half of PtFe particles encapsulated in carbon survived

Compared with Pt/C catalyst
- higher mass-specific activity
- much higher area-specific activity
- good stability by AST test.
Carbon-film encapsulated iron based catalysts (CF-Fe)

▲ The nature of active sites for CF-Fe catalysts is still unclear
▲ FeNPS, Fe₃C, Fe-N₄, Fe/Fe₃C

Financial support
- Danish Council for Strategic Research
  - 4M Center
  - Non-Precious
- the PSO – F&U Foundation
  - CatBooster
  - UpCat
<table>
<thead>
<tr>
<th>Year</th>
<th>temp. °C</th>
<th>Structure*</th>
<th>Characterization</th>
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<tbody>
<tr>
<td>2013, Chung et al.</td>
<td>950</td>
<td>Fe@CNT/CNP(N)</td>
<td>ORR-alkali</td>
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<tr>
<td>2013, Deng et al.</td>
<td>350, 600</td>
<td>Fe@CNT; Fe@CNT(N)</td>
<td>ORR-acid</td>
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<td>2015, Yang et al.</td>
<td>800</td>
<td>Fe₂C@CNT</td>
<td>ORR-alkali@acid</td>
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<tr>
<td>2014, Deng et al.</td>
<td>425~600</td>
<td>CoNi@NC</td>
<td>HER-acid</td>
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<td>2016, Cui et al.</td>
<td>700</td>
<td>Fe@NC</td>
<td>OER-alkali</td>
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<td>2015, Wei et al.</td>
<td>800 ~ 950</td>
<td>Fe₂C@C-FeNₓ</td>
<td>ORR-alkali@acid</td>
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<td>2014, Yang et al.</td>
<td>700, 800</td>
<td>Fe₂C@C</td>
<td>ORR-acid@alkali</td>
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<tr>
<td>2015, Tavakkoli et al.</td>
<td>1100</td>
<td>Fe@C</td>
<td>HER-acid</td>
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<tr>
<td>2015, Strickland et al.</td>
<td>1050</td>
<td>Fe-FexC@CNₓ</td>
<td>ORR-acid@alkali</td>
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*Structure*: Fe@CNT, Fe@CNT(N), Fe@CNT(N), Fe₂C@CNT, CoNi@NC, Fe@NC, Fe₂C@C-FeNₓ, Fe₂C@C, Fe@C, Fe-FexC@CNₓ

*Characterization*: ORR-alkali, ORR-acid, ORR-alkali@acid, HER-acid, OER-alkali, ORR-alkali@acid, ORR-acid@alkali, HER-acid, ORR-acid@alkali