Synthesis of nitrogen doped graphene derivatives for new renewable nano structured membranes used for direct alkaline ethanol fuel cell

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PhD in Material Science
Outline

- Abalonyx AS
- NanoElMem project
- Nitrogen Doping
- Results and Discussion
- Summary
Location

Labs and offices at Sintef, Oslo, Norway

Production site at Tofte, Norway
Graphene Oxide (GO)

Graphite Oxide

Reduced Graphene Oxide (rGO)

Graphene Oxide

Products
Participation in EU projects

• NanoeElMem

Designing new renewable nano-structured electrode and membrane materials for direct alkaline ethanol fuel cell

M-era.Net Funded in 2017
## NanoElMem Partners

<table>
<thead>
<tr>
<th>Coordinator (P1):</th>
<th>Partner 2:</th>
<th>Partner 3:</th>
<th>Partner 4:</th>
<th>Partner 5:</th>
</tr>
</thead>
<tbody>
<tr>
<td>University of Maribor (UM)</td>
<td>University of Nova Gorica (UNG)</td>
<td>Abalonyx</td>
<td>Norwegian University of Science &amp; Technology (NTNU)</td>
<td>Chang Gung University (CGU)</td>
</tr>
<tr>
<td>Slovenia</td>
<td>Slovenia</td>
<td>Norway</td>
<td>Norway</td>
<td>Taiwan</td>
</tr>
</tbody>
</table>

- **Emphasis on:**
  - Platinum (Pt)-free anode catalysts
  - Nano-composite membranes

**Abalonyx + University of Maribor**
The introduction of N into graphene can modify the local electronic structure.

0.6 at% of N doping  
4 times higher electrical conductivity

Both **graphitic (N3) and pyridinic (N1)** have been suggested to facilitate ORR*  

*oxygen reduction reaction

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*N bonding Configurations*

Wei et. Al. *Nano Lett.* **2009**, 9, 1752–1758
Results and Discussion
(Synthesis)

N doped GO

• 1- Ultrasonic treatment
  A simple, rapid and scalable wet-chemical method
  Parameters: **Time** and **Temperature**.

• 2- Plasma treatment
  Exposure to NH$_3$ gas at room temp
  Parameters: **Exposure time** and **Plasma strength**
Results and Discussion (Characterizations)

**X-ray diffractometry (XRD)**

- GO peak at around 11°
- NGO peak with a slight downshift
- Expansion of an interlayer distance as a result of insertion of N atoms
Results and Discussion (Characterizations)

Fourier transform infrared (FTIR)

GO: The peaks at around 1722, 1618, and 1055 cm\(^{-1}\) correspond to the stretching vibrations of C=O, C=C, and C–O groups.

NGO: The intensity of the C=O peak significantly reduced and meanwhile, two new bands at about 1400 and 1250 cm\(^{-1}\) appeared that originated from C=N and C–N stretching vibrations, respectively.
Results and Discussion (Characterizations)

**X-ray photoelectron spectroscopy (XPS)**

The wide-survey spectra shows presence of N in addition to C and O after doping in NGO samples.
Results and Discussion (Characterizations)

XPS Calculations

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at.%)</th>
<th>O (at.%)</th>
<th>N (a.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>66.79</td>
<td>30.89</td>
<td>0.3</td>
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<tr>
<td>Ultrasonic NGO</td>
<td>72.94</td>
<td>23.62</td>
<td>3.44</td>
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<tr>
<td>Plasma NGO</td>
<td>74.68</td>
<td>19.91</td>
<td>5.41</td>
</tr>
</tbody>
</table>

Around 50% of N belongs to **pyridinic** (N1) and **graphitic** (N3) that facilitate oxygen reduction reaction (ORR).

<table>
<thead>
<tr>
<th>N configuration</th>
<th>% in total N</th>
<th>Amount in at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 (pyridinic)</td>
<td>28.16</td>
<td>1.03</td>
</tr>
<tr>
<td>N2 (pyrrolic)</td>
<td>51.46</td>
<td>1.9</td>
</tr>
<tr>
<td>N3 (graphitic)</td>
<td>20.38</td>
<td>0.75</td>
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</table>
N doped rGO

• 1- Thermal annealing

The annealing temperature and the nature of the N sources (precursors).

Melamine (MA) used as N precursor with different ratios
Heat treated at 450°C and at 900°C

• 2- Plasma treatment

Exposure to NH₃ gas at room temp

Parameters: Exposure time and Plasma strength
Results and Discussion (Characterizations)

X-ray diffractometry (XRD)

The degree of crystallinity (peak intensity) of NrGO increases with increasing the temperature. The peak was shifted to a higher 2θ degree, implying a better reducibility.

Both rGO and NrGO show a broad peak placed at around 2θ = 24°. The peak of NrGO show a broader width and weaker intensity.
The peaks corresponding to the oxygen functionalities, such as the C–O and C=O, decreased dramatically. Two new bands at about 1400 and 1250 cm⁻¹ appeared that originated from C=N and C–N.
Results and Discussion (Characterizations)

X-ray photoelectron spectroscopy (XPS)

The wide-survey spectra shows presence of N in addition to C and O after doping in NrGO samples.
### Results and Discussion (Characterizations)

#### XPS Calculations

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>C (at.%)</th>
<th>O(at.%)</th>
<th>N(at.%)</th>
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<tbody>
<tr>
<td>rGO</td>
<td>86.47</td>
<td>13.09</td>
<td>-</td>
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<tr>
<td>Plasma NrGO</td>
<td>82.94</td>
<td>13.58</td>
<td>3.47</td>
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<tr>
<td>MA GO 1:1 450°C</td>
<td>80.11</td>
<td>4.39</td>
<td>15.50</td>
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<tr>
<td>MA GO 3:1 450°C</td>
<td>67.69</td>
<td>2.95</td>
<td>29.34</td>
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<tr>
<td>MA GO 1:1 900°C</td>
<td>93.55</td>
<td>1.33</td>
<td>5.12</td>
</tr>
<tr>
<td>MA GO 3:1 900°C</td>
<td>92.63</td>
<td>1.77</td>
<td>5.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>N1 %</th>
<th>N2 %</th>
<th>N3 %</th>
<th>N4 %</th>
<th>N(at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NrGO Plasma</td>
<td>15.05</td>
<td>53.07</td>
<td>31.88</td>
<td>-</td>
<td>3.47</td>
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<tr>
<td>MA GO 1:1 450°C</td>
<td>39.7</td>
<td>33.6</td>
<td>21.7</td>
<td>4.95</td>
<td>15.50</td>
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<tr>
<td>MA GO 3:1 450°C</td>
<td>50.76</td>
<td>24.55</td>
<td>19.03</td>
<td>5.67</td>
<td>29.34</td>
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<tr>
<td>MA GO 1:1 900°C</td>
<td>31.88</td>
<td>40.17</td>
<td>14.48</td>
<td>13.47</td>
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<tr>
<td>MA GO 3:1 900°C</td>
<td>33.36</td>
<td>32.27</td>
<td>14.9</td>
<td>19.47</td>
<td>5.60</td>
</tr>
</tbody>
</table>
Composite membrane with NGO

CS-90
0.01 % MA-GO (3:1, 900 °C)
Summary

- Abalonyx is producing GO and rGO in large scales.
- The energy section might be taught as a potential candidate for graphene commercialization.
- NanoElmem seeks for solutions to enhance performance of fuel cells by N doping of GO.
Do you have any questions?

THANK YOU FOR YOUR ATTENTION!

ACKNOWLEDGEMENTS
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